Optical Superposition

The sec-octyl dimethoxysuccinates and the sec-octyl tartrates

together with Notes on the Separation of the

"Fusel-oil" Amyl Alcohols.

Thesis

by

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STUDIES IN OPTICAL SUPERPOSITION

The Sec. Octyl dimethoxysuccinates and the d-Sec. Octyl tartrates

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Vant Hoff's so-called Principle of Optical Superposition states that in an optically active compound containing more than one asymmetric carbon atom the part of the rotation due to a given asymmetric atom is independent of the configuration of the groups around the other asymmetric atoms of the molecule. When it is considered to what an extent the properties of an organic compound are determined by the mere arrangement of its constituent groups, the validity of this Principle at once appears doubtful, but the Principle is often assumed to be true, and that in spite of the fact that all definite experimental work that has been done upon it has shown it to be false. It has been shown by Patterson and his co-workers (J.C.S. 1906, 89, 1884 and 1915, 107, 142) that the results which were accepted as proof of this Principle, notably those of Guye and of Walden had really no bearing on the subject as their method of proof eliminated the effects of optical superposition.

The problem is difficult to attack directly and the most suitable method has been shown by Patterson (J.C.S. 1907, 91, 705) to be the study of the rotations of the compounds obtained by

combining with an active radicle the three forms of a substance capable of existing in a d., an l, and an i variety; then, if the rotation of the i-compound is not equal to the mean of the rotations (under the same conditions) of the d- and l- compounds the Principle of Optical Superposition is disproved; but it must be noted that if the rotation of the i-compound does, in a particular case, equal the mean of the rotations of the d- and l- compounds, the Principle of Optical Superposition is not necessarily proved, and further, if the rotation of the i compound approximates closely to the mean of the rotations of the other two, it does not follow that the Principle holds approximately in this case. For example, if the Principle of Optical Superposition holds, the rotations of the esters of an optically active alcohol and d-, l- and i- tartaric acids could be represented as follows:-

I		II		III	
COOR	+ a	COOR	+ a	COOR	+ a
H-C-OH	+ b	HO-C-H	- b	H-C-OH	o
HO-C-H	+ b	H-C-OH	- b	H-C-OH	o
COOR	+ a	COOR	+ a	COOR	+ a
d- acid		l- acid		i- acid	

Rotation of I = 2a +2b

Rotation of II = 2a -2b

Mean of rotations of I and II = 2a
Rotation of III = 2a

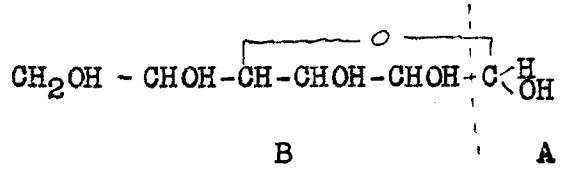
where a and b are the rotation-values of the asymmetric carbon atoms shown.

If the Principle does not hold then a and b will not be the same in the three compounds, and the rotation of III will not, in general, equal the mean of the rotations of I and II; but the changes in the values of a and b due to the rearrangement of the groups attached to the asymmetric carbon atoms may in some cases counterbalance, and mask the effects of optical superposition; it might thus happen that the rotation of III was equal to, or almost equal to, the mean of the rotations of I and II even if the Principle of Optical Superposition were widely departed from.

The results obtained by this method for the three di-menthyl di-acetyl tartrates (J.C.S. 1906, 89, 1884; 1907, 91, 705) and for the l-menthylamine tartrates and the l-amyl dimethoxysuccinates (J.C.S. 1915, 107, 142) were out of agreement with the requirements of the Principle, as were also the results of Tschugaeff and Glebko (Ber. 1907, 46, 2752) for the l menthylurethanes derived from the ethyl esters of d, of l- and of i- tartaric acid, while the observation of Walden (Zeit. physik. Chem. 1896, 20, 377) that the molecular rotation of di-l-amyl i-tartrate exceeds that of di-l-amyl dl-tartrate supports the same view. Although

these results all contradict the Principle of Optical Superposition it is still often assumed to be true, and deductions have been drawn from it. This is the case with recent work by Hudson, who has shown that certain numerical relationships exist in the rotations of substances in the sugar group. Since Hudson's results have been taken as proof of the Principle, it will be as well to consider what bearing they really have on the subject.

Hudson's argument is, that if the two known modifications of glucose are stereoisomers of the formula



then if the rotation value of the aldehyde carbon atom be +A, for one of the stereoisomers, and the rotation-value of the rest of the molecule be +B - the rotation of the whole molecule being A + B - then, if the Principle of optical Superposition holds, the rotation value of the aldehyde carbon atom in the other modification will be - A, and the rotation of the whole molecule - A + B. The difference between the rotations of the α and β forms will be 2A, and will be constant for all the aldehyde sugars, and for all their derivations in which the added substance is not joined directly to the aldehyde carbon atom. Some of his data are given in Table I.

TABLE I

	α form		β form		
	[α]	[M]	[α]	[M]	Δ[M]
d Glucose[1]	109°	196°	20°	36°	160°
d galactose[1]	140	252	53	95	157
l arabinose[1]	76	114	184	276	-162
d lactose[1]	86	294	35	120	174
d Mannose[2]	+34	+61.2	-17	-30.6	91.8
d Lyxose[2]	5.5	8.2	-36	-54.0	62.2
l Rhamnose[2]	-7.7	-12.	+54	+88.	-100
		---			
d glucose pentacetate[3]		396		15	381
d lactose octacetate[3]		365		-29	394
d maltose octacetate[3]		830		425	405
d Cellose octacetate[3]		278		-102	380
d Mannose pentacetate[3]		214		- 98	312
d Galactose pentacetate[3]		416		89	327
l arabinose tetracetate[3]		134		468	-334

1. J. Amer. C. S. 1909, 31, 71
2. J. Amer. C. S. 1917, 39, 1035
3. J. Amer. C. S. 1918, 40, 992.

Similarly it is shown that the sum of the molecular rotations of the α and β forms of d glucose, and of its derivatives in which only the end asymmetric carbon atom is affected should be constant (= 2B).

TABLE II.

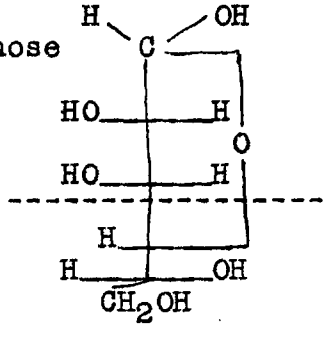
	α form		β form		
	[α]	[M]	[α]	[M]	Σ[M]
d glucose[1]	109	196	20	36	232
methyl d glucoside[1]	157	305	-32	-62	243
ethyl d glucoside[1]	151	314	-30	-62	252

From the figures in Table I, and from others of a similar nature, Hudson concludes that the rotation value of the aldehyde carbon atom is constant, and independent of the configuration of the groups around the other asymmetric carbon atoms. Regarding this conclusion the following points may be noted.

It is an extremely difficult operation to determine the initial rotation of a substance, such as α or β d-glucose, which so quickly undergoes muta-rotation; the initial value having to be determined by extrapolation to zero time. This is indeed indicated by the fact that in one place Hudson gives the specific rotation of α d-glucose as 109° and of the β form as 20° (J.A.C.S. 1909, 31, 71) whilst in another place he gives the specific rotation of the α form as 113.4° and that of the β form as 19° (J.A.C.S., 1917, 39, 1035); the difference between the molecular rotations becoming 169° instead of 160°. If the possible error is of this magnitude in each case then the results might not be sufficiently accurate to show the effects of optical superposition.

The differences found for the first four sugars in Table I vary among themselves by about 10%, which is too large a difference to be ignored; while the differences found for the acetates (Table I) also vary among themselves by over 20%. For d Mannose, d Lyxose and l Rhamnose some of the data have been calculated by Hudson by an indirect method, depending on the rate of solution of the stable form, which is not likely to give very accurate results, but even if the data are only approximately correct they are obviously completely out of agreement with the requirements of the theory. Hudson points out that these sugars have all the same configuration from the $\chi\gamma$ carbon upward and suggests that the exceptional values obtained are due to this particular configuration. But if this configuration caused a change in the rotation value of the aldehyde carbon atom the Principle of Optical Superposition, on which the theory of this numerical relationship depends, is violated.

eg. d Mannose



That the differences found for some of the sugars do conform to the requirements of the theory is not a proof of the Principle of Optical Superposition, since the mutual influences of the various active groups might counterbalance and give a constant difference between the rotations of the α and β forms, even

if this difference were not especially related to the rotation value of the aldehyde carbon atom.

From the figures given in Table II it is concluded that for all the derivatives of d-glucose in which only the end asymmetric carbon is affected the sum of the molecular rotations of the two stereoisomers is the same as the sum of the molecular rotations of α and β d-glucose; this sum being twice the rotation value of the remainder of the molecule (part B above), similar data are given for d-galactose and d-xylose and their derivatives. This would lead, not to the Principle of Optical Superposition, but to the Principle that the rotation value of the remaining active groups in a molecule is unaltered by a change in the groups attached to one of the asymmetric carbon atoms. The same principle would be required, in addion to the Principle of optical Superposition, if the rotation value of the aldehyde carbon atom is the same for the pentoses as for the hexoses and even for the disaccharides and if the rotation value for the end asymmetric carbon atom is the same, for example for d-glucose pentacetate as for d-lactose octacetate and l-arabinose tetracetate (Table I). It is to be noted that the agreement of the experimental results with the theory is as good in these cases as in those which really have to do with optical superposition only.

It is not clear whether Hudson himself considers his results to prove the Principle of Optical Superposition. In one of his earlier papers he says:- "Although there may be some doubt as to

whether the principle holds exactly it seems to the writer that the experimental evidence on it that has been discussed by Rosanoff (J.A.C.S. 1906, 28, 525, 1907, 29, 356) clearly shows that it holds closely. Also it seems quite unlikely that the simple numerical relationships that are shown in the present article, and which are based on the assumption of the above principle, could exist if the principle did not hold at least closely. There is certainly a great need for exact experimental evidence on this principle of optical superposition which is fundamental to the development of stereochemistry." (J. Amer. C. S. 1909, 31, 68 note). Later, however, (J. Amer. C.S. 1917, 39, 462), Hudson calculates the actual rotation value due to each of the asymmetric carbon atoms in the phenylhydrazides of certain acids of the sugar group, and this calculation depends on the Principle holding exactly.

Now, when it is considered that the length of the chain of carbon atoms (part B above) has so little effect on the sum of the rotations of the α and β forms, it is scarcely to be expected that the effects of Optical Superposition will be any more apparent. It is seen above that in the case of mannose and glucose, where the complication due to difference in length of the chain of carbon atoms does not arise, there is a wide departure from the requirements of the principle. Regarding the values for the acetyl derivatives of these sugars, Hudson

says "There is thus some lack of agreement between these values corresponding to 17° in specific rotation, which suggests that the change from the glucose chain, ~~to that~~ of rotation B, to the mannose chain, of rotation B^1, may somewhat change the value of A." (J. Amer. C.S. 1915, 37, 1282). As is already pointed out the agreement in some cases of the experimental results with the theory does not prove the Principle of Optical Superposition and, therefore, since in most cases the requirements of the theory are departed from to some extent and sometimes to a very considerable extent, the only valid conclusion that can be drawn from Hudson's results is that the Principle does not hold.

To obtain further evidence on this question of optical superposition the di-sec-octyl esters of d, of l and of i-dimethoxysuccinic acids were prepared and examined polarimetrically; and di-d-sec-octyl i-tartrate was prepared to complete the series of sec-octyl tartrates.

SEC-OCTYL DIMETHOXYSUCCINATES

The resolution of the sec-octyl alcohol was carried out as described by Pickard & Kenyon (J.C.S. 1907, 71, 2058), 1922, 121, 2540); the modification of the method described by Kenyon in the second of these papers, being adopted. The pure laevo alcohol, which was first used, boiled at 80°/11 mms. and had the

rotation $\alpha^{16^\circ}_{5461}$ (200 mms.) = -19.42°, the value given by Pickard and Kenyon being -19.40°. The alcohol was therefore considered to be pure.

The dimethoxysuccinic acids were prepared by the method described by Patterson & Patterson (J.C.S. 1915, 107, 142) the dextro acid from methyl d-tartrate, and the other two from the silver salts of l- and of i- tartaric acids. The d-dimethoxy-succinic acid used, after recrystallisation from a mixture of acetone and benzene melted at 155° and had the rotation $[\alpha]^{16^\circ}_{5461}$ = + 86.93° (in water c = 1.7831), l dimethoxy-succinic acid melted at 154° and had the rotation $\alpha^{16^\circ}_{5461}$ = -86.93 (in water c = 1.783); the i dimethoxy succinic acid melted at 161°. The esters were prepared by passing dry hydrogen chloride through a mixture of one molecular proportion of the acid and about 4 of the alcohol, for 16 hours, keeping the temperature between 80° and 90° C. The excess of alcohol was distilled up to 100°/40 mms., the residue dissolved in benzene, and the solution washed with dilute sodium carbonate solution, and with water. After drying with calcium chloride the bulk of the benzene was removed, the residue distilled under 4 mms. pressure, and the main fraction redistilled and collected in two fractions. After the second distillation the rotation of the two fractions was generally practically the same, and the substance therefore considered to be pure.

The rotation of these esters was then examined at different temperatures and for different colours of light, both in the homogeneous state and in solution. The experimental data are collected at the end of the paper; as far as the question of optical superposition is concerned they may be summarised as follows:-

TABLE III.

ROTATIONS OF HOMOGENEOUS ESTERS AT DIFFERENT TEMPERATURES

$[\alpha]^{t^\circ}_{5461}$

Temperature t°	l Sec-Octyl l dimithoxy succinate	l Sec-Octyl d dimithoxy succinate	Mean	l Sec-Octyl i dimethoxy succinate	Difference
0°	-77.6°	+48.3°	-14.65°	-14.18°	0.47°
50°	74.9	50.4	12.25	11.90	0.35
100°	72.3	51.4	10.45	10.10	0.35
150	69.5	51.0	9.25	8.95	0.30

It will be noted from these figures that the rotation for the esters of the i acid is different from the mean of the rotations of the esters of the d- and l- acids. The difference is only slight, however, and perhaps not far outside the limit of the experimental error. The fact that the difference varies consistently with change of temperature and would probably be in the opposite sense at higher temperatures favours the view that the results are not affected by any experimental error sufficient to obscure the effect of superposition.

Table IV shows how the difference in rotation varies with change of wave length for the homogeneous esters.

TABLE IV

Specific Rotations t = 20°

λ	l Sec-Octyl l dimethoxy succinate	l Sec-Octyl d dimethoxy succinate	Mean	l Sec-Octyl i dimethoxy succinate	Difference
4358.3	-123.4	+80.25	-21.67	-20.50	1.17
4959.7	95.0	61.80	16.6	16.20	0.40
5460.7	76.7	49.3	13.7	13.15	0.55
5790.3	67.4	43.5	11.95	11.60	0.35
6234.3	58.4	37.4	10.5	10.15	0.35
6716.3	49.9	32.1	8.9	8.79	0.11

The esters were then examined as regards rotation in alcohol, o-nitrotoluene and acetylene tetrachloride at various temperatures and for different colours of light. Table V shows the data obtained in these three solvents at a concentration c = 5 and for the temperature 0°.

TABLE V

α 0° 5461

Physical Condition	I l Sec Octyl l dimethoxy succinate	II l Sec Octyl d dimethoxy succinate	III Mean of I and III	IV l Sec Octyl i dimethoxy succinate	V Difference ~~V-VI~~ III − IV
Homogeneous	-77.60	+48.30	-14.65	-14.18	-0.47
In alcohol	-77.07	+52.67	-12.20	- 9.52	-2.68
In o.Nitro-toluene	-96.0	+85.00	- 5.5	-2.25	-3.25
In S.Tetra-chlorethane	-61.4	+40.58	-10.41	-8.65	-1.76

It will be observed that the differences (Col. V) between the rotation for the i ester and the mean (Col. III) of the rotations for the d and l esters is decidedly greater in solution than in the homogeneous condition. In o-nitrotoluene it amounts to 3.25° which, whilst not large in comparison with the range of 181° over which the rotation of the esters of the d- and l-acids extend, is numerically greater than the actual rotation (2.25°) of the ester of the i acid. In the other two solvents tried the difference also seems clearly to be greater than the probable experimental error. The behaviour on change of temperature and colour of light are nearly the same as for the homogeneous substance; in Table VI are given the data for different temperatures for the solutions in O.nitrotoluene.

TABLE VI $[\alpha]^{t^\circ}_{5461}$ NITROTOLUENE SOLUTIONS

t°	l Sec-Octyl i dimethoxy succinate	l Sec-Octyl d dimethoxy succinate	Mean	l Sec-Octyl i dimethoxy succinate	Difference
0°	-96.0	+85.0	-5.5	-2.25	3.25
25°	89.5	78.6	5.45	3.72	2.73
50°	85.0	72.6	6.2	4.55	1.65
75°	80.5	67.4	6.55	4.85	1.70
100°	77.0	64.6	6.2	4.75	1.45

It will be noted that the differences in O-nitrotoluene solution like those for the homogeneous ester decrease fairly

regularly with rise of temperature, and would probably be in the opposite sense at still higher temperatures. If the differences obtained were due to any experimental error, this behaviour would scarcely be expected.

The experiments detailed above involve the resolution of two potentially active compounds, sec-Octyl alcohol and racemic acid, as well as the preparation of i-tartaric acid, and since on this account the experimental error might be considerable it was thought worth while to corroborate the results by preparing the esters corresponding to those described but from d sec-octyl alcohol instead of from l sec-octyl alcohol. The d sec-octyl alcohol had a slightly higher rotation than the laevo, namely $\alpha^{16^\circ}_{5461}$ (200 mms) = + 19.45° as against -19.42° for the laevo alcohol and 19.40° of Pickard and Kenyon.

The various esters were prepared and purified as before, but in smaller quantity and were not so completely examined. Table VII gives a comparison of the results obtained.

TABLE VII

Observed Rotations - Hg green - 100 mms. at 17° C.

	l-acid	d-acid	Mean	i-acid	Δ
Di l-sec-octyl esters of dimethoxy succ. acids	-74.16	+47.40	-13.38	-12.92	-0.46
	d-acid	l-acid			
Di d-sec-octyl esters	+74.72	-46.61	+14.05	+13.48	+0.57

Specific Rotations in Alcohol Solution (C = 5) at 16° C.(Approx.) Hg. green

	l-acid	d-acid	Mean	i-acid	Δ
l-sec-octyl esters	-75.73	+53.04	-11.34	-8.72	-2.62
	d-acid	l-acid			
d-sec-octyl esters	+77.11	-53.0	+12.05	+9.33	+2.72

Specific Rotations in O-nitrotoluene solution (C = 5) at 14° C. Hg green

	l-acid	d-acid	Mean	i-acid	Δ
l-sec-octyl esters	-92.4	+81.25	-5.57	-3.12	-2.45
	d-acid	l-acid			
d-sec-octyl esters	+93.4	-80.7	+6.35	+3.10	+3.25

Specific Rotations in S-Tetrachlorethane solution (c=5) at 18°C.

	l-acid	d-acid	Mean	i-acid	Δ
l-sec-octyl esters	-61.5	+41.6	-9.95	-8.55	-1.40
	d-acid	l-acid			
d-sec-octyl esters	+61.92	-40.5	+10.71	+8.35	+2.36

In the table the data for observed rotation are compared in the case of the homogeneous esters as the densities of the d-sec-octyl esters were not determined; any difference in the specific rotations due to difference in the density would be negligible.

It will be seen that the results agree closely with those obtained with the l-alcohol. The difference between the rotation (λ = 5461) of the ester of the i acid and the mean of the rotations for the homogeneous esters of the d and l-acids in the second series of experiments is 0.57° as against 0.46°; in alcohol solution it is 2.72° as against 2.62°; in nitrotoluene 3.25° as against 2.45°; and in s-tetrachlorethane it is 2.36° as against

1.40°. The behaviour of the two series is thus entirely consistent, and although the departure from the requirements of the principle of optical superposition is small, compared with what it was found to be in some of the series mentioned in the first part of the paper, it appears to be quite definite.

THE SEC-OCTYL TARTRATES

The sec-octyl esters of dextro and of laevo tartaric acids have been prepared by Pickard & Kenyon (J.C.S. 1911, 99, 68), and their rotations determined, but these authors found that the sec-octyl ester of i-tartaric acid decomposed on distillation. Since the dimethoxysuccinates distilled easily to give clear oils after washing free from all acid and acid ester, it was thought worth while to find if sec octyl i-tartrate could be distilled after similar treatment.

In this way d-sec-octyl i-tartrate was obtained as a solid (M.P. = 33°) distilling at 208° (about 4 mms) and its rotation was examined for the six different colours of light shown, the value for the D line being obtained by interpolation. By cooling the melted solid slowly it was possible to examine the rotation at 17° through the supercooled liquid.

The figures given by Pickard and Kenyon (loc. cit.) are as follows:-

	$[\alpha]_D^{17^\circ}$	d-Tartaric acid	l-Tartaric acid
d methyl n-hexyl carbinol		+24.06	+2.06
l methyl n-hexyl carbinol		- 1.93	-24.20

	r-Tartaric acid
d methyl n hexyl carbinol	+14.12°

From these figures we obtain:-

Mean of rotations of d sec-octyl d tartrate and d sec-octyl l tartrate = + 13.06°

Mean of rotations of l sec octyl l tartrate and l sec octyl d tartrate = - 13.065°

Specific Rotation found for d-sec-octyl i-tartrate $[\alpha]_D^{17^\circ}$ = +0.42°

To find if the low rotation value of the i tartrate were due to racemisation of the alcohol 5 grams of the ester were hydrolysed by boiling with potassium carbonate solution; the recovered alcohol had the rotation $\alpha_{5461}^{18.5^\circ}$ (30.48 mms) = +2.64, for the pure alcohol the corresponding value is + 2.95°. The slightly lower value for the rotation is probably due to the difficulty of purifying completely the small quantity (about 2 ccs) of alcohol obtained from the hydrolysis. This alcohol may however be slightly racemised and as some decomposition took place during the hydrolysis with K_2CO_3, the mixture darkening, any racemisation probably took place during this operation. Since the rotations, of the d and l sec-octyl esters of d and of

l tartaric acids, obtained by Pickard & Kenyon agree so well with each other it is unlikely that any racemisation occurs during the preparation of the ester. In any case any impurity in the alcohol contained in the ester could not account for the difference (13.06-0.42) observed between the rotation of the i ester and the mean of the rotations of the d and l esters, so that in this series the requirements of the principle of optical superposition are clearly departed from to a considerable extent.

From the above results it is therefore seen that the so-called Principle of Optical Superposition is invalid; in some cases, as with the sec-octyl dimethoxysuccinates the deviation from the requirements of the principle may be very slight and possibly scarcely beyond the limits of experimental error, but in others as is the case with the d-sec-octyl tartrates the deviation is quite distinct. As is already pointed out above the effects of the various asymmetric groups on each other may counterbalance and give results which appear to confirm the Principle, but one well established case in which the requirements of the Principle are widely departed from is sufficient to disprove its validity.

EXPERIMENTAL

1-sec-Octyl d-dimethoxysuccinate was prepared from 10 gmms. d-dimethoxy-succinic acid and 35 grams l-sec-octyl alcohol. Dry hydrogen chloride was passed for 16 hours through the mixture which was kept at 80-90° C. The resulting mixture was distilled to 100°/40 mms. to remove excess alcohol and the residue was then distilled under 4 mms. pressure. Since the distillate had a distinctly acid reaction, probably containing excess dimethoxy-succinic acid or acid ester, and was turbid, it was dissolved in benzene, neglecting a small first fraction and washed with dilute sodium carbonate solution and with water. The benzene solution was dried with calcium chloride and distilled to 100°/40 mms; the remainder was then distilled under 4 mms. pressure, a small first fraction was neglected and the remainder redistilled. It boiled at 196°/4 mms. A small first fraction had the rotation $\alpha^{13.5^\circ}_{5461} = +47.5^\circ$ and the main portion (about 12 grams) had the rotation $\alpha^{13.5^\circ}_{5461} = +47.415$.

Densities:-

t	0°	12.2°	13°*	42.5°*	43°	63°*
d	.9794	.9692	.9690	.9453	.9449	.9292
t	78.2°*	68.8°	100°*	147.5°		
d	.9171	.9244	.9001	.8649		

*Experimental values.

l-sec-octyl d-dimethoxysuccinate

λ	t	α (50 mms)	$[\alpha]$	$[M]$
	0°	+15.328	+31.30	+125.8
6716.3 (r_1)	12.5	15.345	31.666	127.3
	43.	15.315	32.42	130.3
	68.8	15.09	32.65	131.3
	100.	14.69	32.62	131.1
	147.5	14.007	32.39	130.2
	0	17.971	36.70	147.5
	12.5	17.985	37.11	149.2
	43.0	17.901	37.89	152.3
6234.3 (r_2)	68.8	17.75	38.40	154.4
	100	17.327	38.48	154.8
	147.5	16.50	38.15	153.4
	0	20.908	42.70	171.7
	12.5	21.01	43.36	174.3
	42.8	20.945	44.33	178.2
5790.3 (y)	68.8	20.758	44.91	180.5
	100.	20.299	45.08	181.2
	147.5	19.401	43.84	176.4
	0	23.635	48.27	194.1
	12.5	23.695	48.88	196.5
	42.8	23.78	50.33	202.2
	68.8	23.535	50.92	204.7
5460.7 (g)	100.	23.06	51.21	205.9
	147.5	22.061	51.01	205.1
	After cooling 18.0	23.67		
	0	29.503	60.24	242.2
	12.5	29.767	61.43	246.9
	43.0	29.84	63.16	253.9
	68.8	29.645	64.14	257.8
4959.7 (b)	100.	29.184	64.81	260.5
	147.5	28.115	65.01	261.3
	0	38.18	77.97	313.4
	12.5	38.478	79.40	321.2
	43.0	39.011	82.57	331.9
4358.3 (v)	68.8	39.002	84.38	339.2
	100.	38.6	85.72	344.6
	147.5	37.295	86.24	346.8

Alcoholic solution p = 6.210 c = 4.996

Densities:- t° 0° 11.5°* 16° 30°* 42.8* 52.8*
d .8185 .8068 .8045 .7925 .7816 .7724

	t°	α (160 mms)	$[\alpha]$	$[M]$
	0°	+ 2.753	+33.84	+ 136.0
r_1	16	2.735	34.22	137.5
	0	3.231	39.49	158.7
r_2	16	3.185	39.85	160.2
	0	3.84	47.00	188.9
y	16	3.742	46.81	188.2
	0	4.285	52.67	211.7
g	16	4.24	53.04	213.2
	0	5.37	66.00	265.3
b	16	5.295	66.24	266.3
	0	6.935	85.24	342.7
v.	16	6.885	86.93	349.5

β-Tetrachlorethane Solution p = 3.1868 c = 5.0065

Densities:-

t°	0°	14.5	30.2*	43.5	53.4*
d	1.5972	1.5759	1.5525	1.5328	1.5179
t	74.5°*	75°	99°*	98.5°	
d	1.4866	1.4853	1.4481	1.4485	

	t°	α(160 mms)	[α]	[M]
r_1	0	+ 2.123	+26.07	+104.80
	14.5	2.185	27.16	109.3
	43.5	2.23	28.53	114.7
	75.	2.186	28.87	116.0
	98.5	2.178	29.49	118.5
r_2	0	2.487	30.54	122.8
	14.5	2.535	31.40	126.2
	43.5	2.565	32.82	131.9
	75.	2.525	33.34	134.0
	98.5	2.50	33.85	136.1
y	0	2.89	35.49	142.7
	14.5	2.97	36.96	148.6
	43.5	2.992	38.28	153.9
	75.0	2.922	38.58	155.1
	98.5	2.95	39.94	160.5
g	0	3.305	40.58	163.1
	14.5	3.328	41.42	166.5
	43.5	3.43	43.89	176.4
	75.0	3.40	44.90	180.5
	98.5	3.35	45.36	182.3
b	0	4.035	49.55	199.2
	14.5	4.18	52.02	209.1
	43.5	4.27	54.64	219.6
	75.0	4.255	56.19	225.9
	98.5	4.212	57.03	229.3
v.	0	5.218	64.07	257.5
	14.5	5.23	65.09	261.7
	43.5	5.568	71.24	286.4
	75.	5.58	73.68	296.2
	98.5	5.545	75.08	301.8

O-Nitrotoluene Solution p = 4.3205 c = 5.002

Densities:-

t° C.	0	17.8	44.5	63*	84*	100
d.	1.1702	1.1314	1.1300	1.1008	1.0916	1.0765
t	42.8*					
d	1.1314					

	t	α (100 mms)	$[\alpha]$	$[M]$
r_1	0	+4.368	+54.00	+217.1
	17.8	4.11	51.64	207.6
	45.	3.67	46.98	188.9
	74.5	3.338	43.85	176.3
	100.	3.055	41.05	172.4
r_2	0	5.13	63.42	254.9
	17.8	4.79	60.18	241.9
	45	4.292	54.95	220.9
	75.	3.882	51.02	205.1
	100.	3.57	47.97	192.8
y	0	6.04	74.66	298.8
	17.8	5.66	71.12	285.9
	44.5	5.05	64.65	259.9
	75.0	4.544	59.85	241.6
	100.	4.254	57.17	229.8
gr.	0	6.895	85.24	342.7
	17.8	6.41	80.54	323.8
	44.5	5.80	74.25	298.5
	75.	5.19	67.20	270.1
	100.	4.795	64.44	259.0
b.	0	8.744	108.09	434.5
	17.8	8.09	101.65	408.6
	45.	7.298	93.43	375.6
	75.	6.56	86.21	346.5
	100.	6.027	80.99	325.5

1-Sec-Octyl 1-dimethoxy succinate was prepared from 10 grams of the acid and 40 grams of the alcohol and was treated exactly as described above. In the final distillation the first fraction had the rotation $\alpha^{16^\circ C}_{5461}$ (100 mms) = -74.22° and the main fraction $\alpha^{17^\circ}_{5461}$ (100 mms) = -74.105°. B.Pt. = 190° (4 mms)

Densities:-

t	0°	14*	43	44.6*	60.5*	77.5
d	.9764	.9653	.9430	.9416	.9291	.9162
t	80.5*	100*	147.5			
d	.9134	.8984	.8613			

	t	α(50 mms)	[α]	[M]
r_1	0	-24.925	-51.06	-205.3
	14	24.088	49.81	200.2
	43	23.099	48.99	196.9
	77.5	21.923	47.861	192.4
	100	21.18	47.15	189.5
	147.5	20.378	47.32	190.2
r_2	0	28.85	59.095	237.5
	14	28.235	58.37	234.6
	43	26.987	57.24	230.1
	77.5	25.535	55.75	224.1
	100.	24.645	54.86	220.5
	147.5	22.63	52.55	211.2
y	0	33.495	68.61	275.8
	14.	32.835	67.53	271.5
	43.	31.535	65.72	264.2
	77.5	29.819	65.09	261.7
	100.	28.66	63.76	256.3
	148	26.439	61.393	246.8
g	0	37.835	77.50	311.6
	14	37.135	76.94	309.5
	43	35.73	75.78	304.6
	77.5	33.82	73.84	296.8
	100.	32.555	72.47	291.3
	147.5	29.995	69.652	280.0
	After cooling 14.5	37.105		

	0	-46.772	-95.81	-385.1
	14	46.15	95.62	384.4
	43	44.545	94.48	379.8
b	77.5	42.08	91.87	369.3
	100.	40.649	90.49	363.8
	147.5	37.498	86.07	345.0
	0	60.506	124.6	500.9
	14	59.66	123.61	496.9
	43	57.605	122.17	491.1
v	77.5	54.94	119.94	482.1
	100.	53.033	118.06	474.6
	147.5	49.038	115.03	462.4

Alcoholic solution p = 6.229. c = 4.997

Densities:-

t°	0	13*	16.5	27*	37.2*	47*
d	.8163	.8052	.8022	.7935	.7846	.7766

	t°	α (160 mms)	$[\alpha]$	$[M]$
r_1	0	-4.173	-51.29	-206.2
	16.5	4.018	50.25	202.2
r_2	0	4.814	59.17	237.8
	16.5	4.627	57.87	232.6
y	0	5.568	68.44	275.1
	16.5	5.380	67.29	270.5
g	0	6.27	77.07	309.8
	16.5	6.055	75.73	304.3
b	0	7.805	95.93	385.6
	16.5	7.513	93.97	377.7
v	0	9.963	122.46	492.3
	16.5	9.626	120.40	484.0

S-Tetrachlorethane solution. p = 3.1896 c = 5.001.

Densities:-

t^o	0	14	15.2*	37.8*	43	56*
d	1.5972	1.5765	1.5747	1.5411	1.5335	1.5138
t^o	71	75*	99*	100		
d	1.4915	1.4853	1.4479	1.4465		

	t^oC	α (160 mm)	$[\alpha]$	[M]
r_1	0	-3.336	-40.92	-164.5
	14	3.285	40.83	164.2
	43	3.17	40.51	162.9
	71	3.007	39.51	158.8
	100	2.917	39.52	158.8
r_2	0	3.85	47.23	189.9
	14	3.785	47.05	189.1
	43	3.628	46.36	186.4
	71	3.38	44.41	178.5
	100	3.368	45.62	183.4
y	0	4.436	54.42	218.7
	14	4.39	54.57	219.3
	43	4.24	53.18	213.8
	71	4.035	53.01	213.1
	100	3.888	52.67	211.7
g	0	5.005	61.40	246.8
	14	4.94	61.40	246.8
	43	4.748	60.67	243.9
	71	4.565	59.97	241.0
	100	4.406	59.68	239.9
b	0	6.154	75.50	303.5
	14	6.084	75.80	304.7
	43	5.815	74.30	298.7
	71	5.666	74.44	299.2
	100	5.51	74.64	300.0
v	0	7.782	95.47	383.8
	14	7.635	94.91	381.5
	43	7.631	97.51	392.0
	71	7.27	95.51	384.0
	100	7.02	95.10	382.3

O-Nitrotoluene solution p = 4.3394 c = 5.005

Densities:-

t	0°	16°	17.5*	42.8°	43.4*
d	1.1702	1.1560	1.1541	1.1312	1.1304
t	61.2*	73.2°	79.8*	100*	
d	1.1137	1.1028	1.0963	1.0765	

	t°	α (160 mms)	$[\alpha]$	$[M]$
r_1	0	-5.035	-61.97	-249.1
	16	4.738	59.17	237.8
	42.8	4.404	56.08	225.4
	73.2	3.992	52.14	209.6
	100	3.75	50.17	201.7
r_2	0	5.782	71.17	286.1
	16	5.52	68.94	277.0
	42.8	5.065	64.50	259.3
	73.2	4.65	60.73	244.1
	100	4.32	57.80	232.4
y	0	6.787	83.54	335.8
	16	6.444	80.47	323.5
	42.8	5.954	75.82	304.9
	73.2	5.408	70.63	283.9
	100	5.035	67.37	270.8
g	0	7.805	96.06	386.2
	16	7.36	91.91	369.5
	42.8	6.775	86.27	387.0
	73.2	6.18	80.71	324.5
	100	5.76	77.07	309.6
b	0	10.026	123.57	497.7
	16	9.495	118.57	476.6
	42.8	8.646	110.10	442.6
	73.2	7.807	101.96	409.9
	100	7.266	97.22	390.8

l sec-Octyl i dimethoxy-succinate was prepared from 10 gmms. i dimethoxy-succinic acid and 35 grams l-sec-octyl alcohol. After passing hydrogen chloride through the mixture for 18 hours, the excess alcohol was distilled off under reduced pressure. The distillate separated into two layers, the lower (aqueous) layer was removed, and the alcohol poured back into the mixture which was again saturated with dry hydrogen chloride (16 hours). This double saturation gave no appreciable increase in the yield of the ester which had still the same turbid appearance, after distillation, as was observed with the two previous esters, and had a distinctly acid reaction. The ester was therefore dissolved in benzene and treated as described above. In the final distillation the first fraction had the rotation $\alpha^{18^\circ}_{5461} = -12.72^\circ$ (100 mms) and the main portion $\alpha^{18.5^\circ}_{5461} = 12.69^\circ$. B.Pt. = 199°-201°/4 mms.

Densities:-	t°	0	16.2	18.5*	41.2*	42	
	d	.9775	.9646	.9627	.9439	.9437	
	t°	60*	73	81*	100*	127.2	150.2
	d	.9294	.9189	.9123	.8973	.8756	.8572

	t	α (50 mms)	$[\alpha]$	[M]
r_1	0	-4.601	-9.41	-39.8
	17	4.29	8.90	35.8
	42	3.845	8.15	32.8
	73	3.387	7.37	29.6
	100	3.035	6.76	27.1
	127.2	2.819	6.44	25.9
	150.2	2.589	6.04	24.3
r_2	0	5.325	10.88	43.7
	16.8	4.935	10.25	41.2
	42.	4.40	9.33	37.5
	73.	3.90	8.49	34.1
	100.	3.495	7.79	31.3
	127.2	3.225	7.37	29.6
	150.2	2.977	6.95	27.9
y	0	6.085	12.45	50.0
	16.2	5.685	11.79	47.4
	42.	5.075	10.76	43.2
	73.	4.475	9.74	39.1
	100.	4.045	9.02	36.2
	127.5	3.695	8.44	33.9
	150.2	3.41	7.96	32.0
g	0	6.925	14.17	56.9
	16.2	6.401	13.27	53.3
	42.	5.73	12.15	48.8
	73.	5.025	10.94	44.0
	100.	4.50	10.03	40.3
	127.5	4.14	9.59	38.5
	150.2	3.815	8.90	35.8
	After Cooling 19.5	6.275		
b	0	8.569	17.53	70.5
	16.8	7.878	16.34	65.6
	42.	7.072	14.99	60.2
	73.	6.164	13.42	53.9
	100.	5.478	12.22	49.1
	127.2	5.071	11.58	46.5
	150.2	4.633	10.81	43.4

	t°	α	$[\alpha]$	$[M]$
	0	10.825	22.148	89.0
	16.5	9.985	20.72	83.3
	42	8.905	18.87	75.8
	73.	7.71	16.78	67.4
v.	100.	6.89	15.36	61.7
	127.2	6.365	14.54	58.4
	150.2	5.766	13.45	53.9

O-Nitrotoluene Solution p = 4.3407 c = 5.003

Densities:-

t	0°	15.8°*	16°	40.8°*	53°
d	1.1702	1.1566	1.1560	1.1332	1.1230
t	65°	78°*	79°	100°	
d	1.1107	1.0976	1.0972	1.0765	

	t°	α (160 mms)	$[\alpha]$	$[M]$
	0	-0.151	-1.86	-7.5
	16	0.197	2.46	9.9
r_1	52	0.260	3.33	13.4
	79	0.265	3.48	14.0
	100	0.274	3.66	14.7
	0	0.16	1.97	7.9
	16	0.218	2.72	10.9
	52	0.28	3.59	14.4
r_2	79	0.30	3.94	15.8
	100	0.297	3.97	15.9
	0	0.164	2.02	8.1
	16	0.247	3.08	12.4
	52	0.319	4.09	16.4
y	79	0.327	4.29	17.2
	100	0.32	4.28	17.2
	0	0.18	2.215	8.9
	16	0.27	3.37	13.5
	52	0.355	4.55	18.3
g	79	0.362	4.75	19.1
	100	0.358	4.79	19.2
	0	0.241	2.97	11.9
	16	0.341	4.26	17.1
	52	0.44	5.64	22.7
b	79	0.476	6.24	25.1
	100	0.468	6.26	25.2

Alcoholic solution p = 6.230 c = 4.9975.

Densities determined:-

t	15°	27°	37.2°	49.5°
d	.8027	.7938	.7853	.7745

	t°	d	α (160 mms)	$[\alpha]$	$[M]$
r_1	0	.8170	-0.561	-6.89	-27.7
	16.8	.8026	0.512	6.28	25.2
r_2	0	.8170	0.619	7.76	31.2
	16.8	.8026	0.555	6.94	27.9
y	0	.8170	0.689	8.46	34.0
	16.4	.8029	0.613	7.67	30.8
g	0	.8170	0.775	9.52	38.2
	16.2	.8032	0.697	8.72	35.0
b	0	.8170	0.886	10.91	43.9
	16.5	.8028	0.849	10.618	42.7
v	0	.8170	1.063	13.056	52.5
	16.5	.8028	0.998	12.48	50.2

S. Tetrachlorethane solution p = 3.1889 c = 5.005

Densities:-

t	0°	15°*	40°*	44.2°	60°*
d	1.5972	1.5751	1.5386	1.5316	1.5088
t	72.5	81°*	100°		
d	1.4890	1.4759	1.4465		

	t	α (160 mms)	$[\alpha]$	$[M]$
g	0°	-0.705°	-8.65°	34.77°
	15	0.690	8.59	34.53
	44.2	0.655	8.38	33.69
	72.5	0.580	7.63	30.67
	100.	0.526	7.13	28.66

d-Sec-Octyl d-dimethoxy-succinate was prepared from 6 grams of the acid and 16 grams of the alcohol, in the same manner as the esters of the laevo alcohol. It distilled at 202°/5 mms, a first small fraction being collected separately; the main portion had the rotation $\alpha^{19^\circ}_{5461} = +74.62^\circ$. This was redistilled and a small first fraction again removed, and the rotation of the main fraction was now $\alpha^{17^\circ}_{5461} = +74.72^\circ$.

d-sec-octyl l-dimethoxy succinate was prepared in the same manner. It distilled at 194°/ about 4 mms and had the rotation $\alpha^{15.5^\circ}_{5461}$ (100 mms) =-46.56. After redistillation the rotation was $\alpha^{17^\circ}_{5461}$ (100 mms) =-46.61

d sec-octyl i dimethoxy succinate distilled at 202°/5 mms and had the rotation $\alpha^{12.5^\circ}_{5461} = +13.71^\circ$. After redistillation the rotation was $\alpha^{13^\circ}_{5461} = +13.67^\circ$.

The rotation of these esters was examined at one temperature only, both in the homogeneous state and in solution; in order to make the comparisons shown in Table VII an allowance was made, where necessary, for the slight changes in temperature required, by assuming that the change in rotation with temperature is the same for these esters as for the corresponding esters of the laevo alcohol. The allowances so made are small and would not affect

the results.

The solvents used for the determination of the rotations in solution in both series were purified carefully; the alcohol being dried with sodium and redistilled, and the O-nitrotoluene and S-tetrochlorethane dried with anhydrous calcium chloride and distilled under reduced pressure. The solutions of the esters of the dextro alcohol were prepared by weighing out, as nearly as possible, 0.25 grams of the ester in a 5 cc. flask and filling up to the mark with the solvent. As a check the solution was then weighed and the specific rotation calculated using the density of the corresponding solution of the 1 alcohol series, the specific rotations so calculated did not differ appreciably from the specific rotations calculated using only the mass per 100 ccs.

	Solvent	C	t°C	$\alpha^{(100\ mms)}_{Hg\cdot green}$	$[\alpha]$
d-sec-octyl	Alcohol	5	16°	-2.65	-53.0
l-dimethoxy-	O-nitrotoluene	5	20°	-3.96	-79.2
succinate	S-Tetrachlorethane	5.008	20°	-2.025	-40.43
d-sec-octyl	Alcohol	5.012	15°	+3.865	+77.11
d-dimethoxy-	O-Nitrotoluene	5.014	14.2°	+4.685	+93.44
succinate	S-Tetrachlorethane	4.992	16°	+3.092	+61.92
d-sec-octyl	Alcohol	5.004	16.5°	+0.467	+ 9.33
l-dimethoxy-	O-Nitrotoluene	5.012	16.5°	+0.16	+ 3.19
succinate	S-Tetrachlorethane	5.008	18.°	+0.418	+ 8.35

Analyses:- About 0.5 grams of each ester was hydrolysed by boiling with a standard solution of caustic soda in methyl alcohol, with the addition of a little water, for about an hour, and the excess caustic soda was titrated with standard HCl solution. N.F. of NaOH solution = .2004.

			Wt. of ester grams	Vol. of NaOH solution used ccs.	Theory requires ccs.
	(ℓ-dimeth:	succinate	0.4200	10.31	10.42
	(d- "	"	0.4825	12.03	11.98
l sec-octyl	(i- "	"	0.4785	11.90	11.95
	(d- "	"	0.4583	11.6	11.4
d sec-octyl	(ℓ- "	"	0.3047	7.66	7.57
	(i- "	"	0.2407	6.07	5.98

Estimation of carbon and hydrogen:-	Carbon	Hydrogen
Theoretical for $C_{22}H_{42}O_6$	65.67%	10.45%
d-sec-octyl d dimethoxy succinate	65.45	10.41
d " " i " "	65.33	10.50
d " " i " "	65.27	10.46
i " " i " "	65.40	10.52

Di-d-sec-octyl i-tartrate was prepared by mixing 10 grams i-tartaric acid with 30 grams d-sec-octyl alcohol, and passing dry hydrogen chloride through the mixture for 20 hours, keeping the temperature between 80° and 90°. The mixture was then distilled to 100°/30 mms to remove excess alcohol. The residue

was dissolved in benzene, and the solution washed with dilute sodium carbonate solution, when a solid* was precipitated. After filtering off the solid, the benzene solution was washed with water, dried with calcium chloride and the bulk of the benzene distilled off. The total residue was then distilled up to 140° (about 4 mms) to remove all excess benzene and alcohol. The ester which remained was distilled in very small quantities at a time under 4 mms pressure; there was some slight frothing at the start of the distillation in each case, but otherwise the liquid distilled easily; and, on standing, the distillate solidified to a mass of soft needles. The combined distillates were re-distilled three fractions being taken. The total yield was about 8 grams.

	B.Pt.(4 mms)	M.P.
1st small fraction	200-208	(about) 30°
2nd " "	208°	33°
Main fraction	208°	33°

Analyses:- Hydrolysis with solution of caustic soda in methyl alcohol. N.F. = .1007.

			ccs.
0.2601 grams	di-sec-octyl tartrate requires	13.80 ccs. Found	13.88
0.2855 "	" " "	15.16 " "	15.15

*This solid was probably sodium-d-sec-octyl tartrate. It was very sparingly soluble in cold water, but readily soluble on heating and crystallised at once, on cooling a warm solution, in glistening plates. 0.1012 gram dissolved in 20 ccs. water at 20° gave a rotation of -0.024° in a 2 dm. tube, whence $[\alpha]^{20°}_{5461}$ = -2.37°.

On hydrolysis with .0994 N. NaOH solution, 0.2013 gram required 7.27 ccs. Theoretical for $NaOOC-(CHOH)_2-COOC_8H_{17}$ is 7.13 ccs.

Rotation of d sec-octyl i-tartrate

Densities:-	t	17°	35.5°*	36.5°	48°*	64°*	85.5°*
	d	.9998	.9849	.9840	.9743	.9618	.9442

*Experimental

	t	Length of tube (mms)	α	$[\alpha]$	$[M]$
r_1	17°	30.478	+0.148	+0.486	+1.82
r_2			+0.14	0.459	1.72
y			0.124	0.407	1.52
g			0.056	0.184	0.688
b			-0.012	-0.039	-0.146
v			-0.448	-0.147	-5.50
r_1	36.5°	30.49	+0.147	+0.490	+1.83
r_2			0.237	0.790	2.98
y			0.212	0.706	2.64
g			0.19	0.633	2.37
b			0.089	0.297	1.11
v			-0.09	-0.303	-1.13

EFFECT OF CHANGE OF TEMPERATURE AND OF SOLVENTS ON THE ROTATION OF THE L-SEC-OCTYL DIMETHOXYSUCCINATES

1-sec-Octyl d-dimethoxysuccinate.

The rotation of the homogeneous ester increases towards a maximum with increase of temperature; the maximum appears at a lower temperature (about 70°C) for red and moves to beyond 150° for blue and violet. Solution in o-nitrotoluene raises the specific rotation at low temperatures, but the rotation decreases fairly rapidly on raising the temperature, and would seem to tend towards a minimum for higher temperatures than those recorded. Solution in S-tetrachlorethane diminishes the specific-rotation without greatly altering the shape of the temperature-rotation curves except that the maximum is moved to a slightly higher temperature (this maximum is not shown in the specific rotations below 100° but is apparent in the observed rotations, and would appear in the specific rotations at a higher temperature). In the general shape of the T-R curves and in the effect of these solvents on its rotation this ester therefore resembles ethyl tartrate to a certain extent (cf. Patterson, J.C.S. 1916, 109, 1141). Graphs I, II and III show the T-R curves for the homogeneous ester and for the solutions, while graph IV shows the T-R curves for one colour of light only for the homogeneous ester and for the solutions in o-nitrotoluene and in s-tetrachloroethane. From

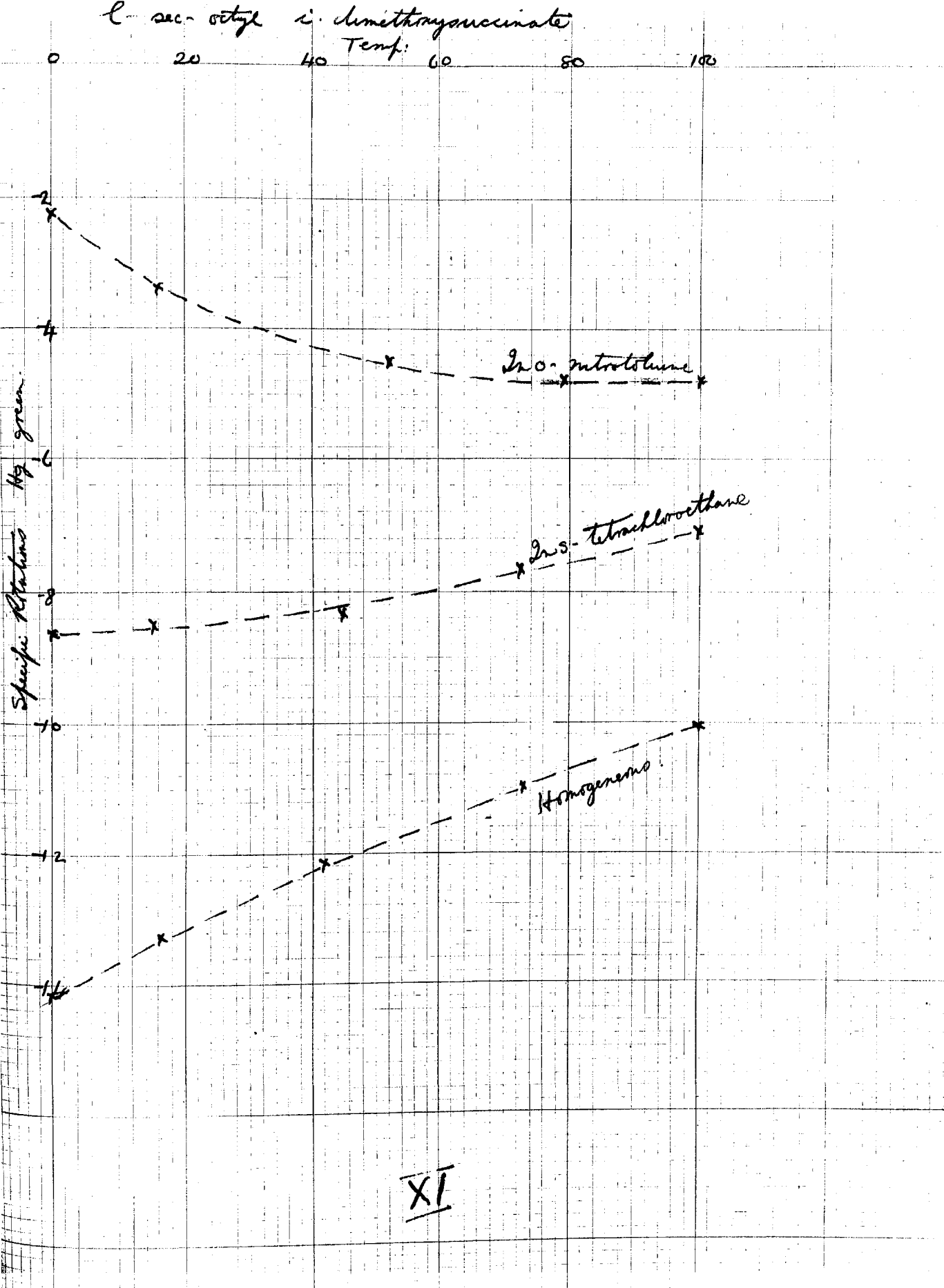
this graph the effect of these solvents can be more clearly seen.

l-sec-octyl l-dimethoxysuccinate.

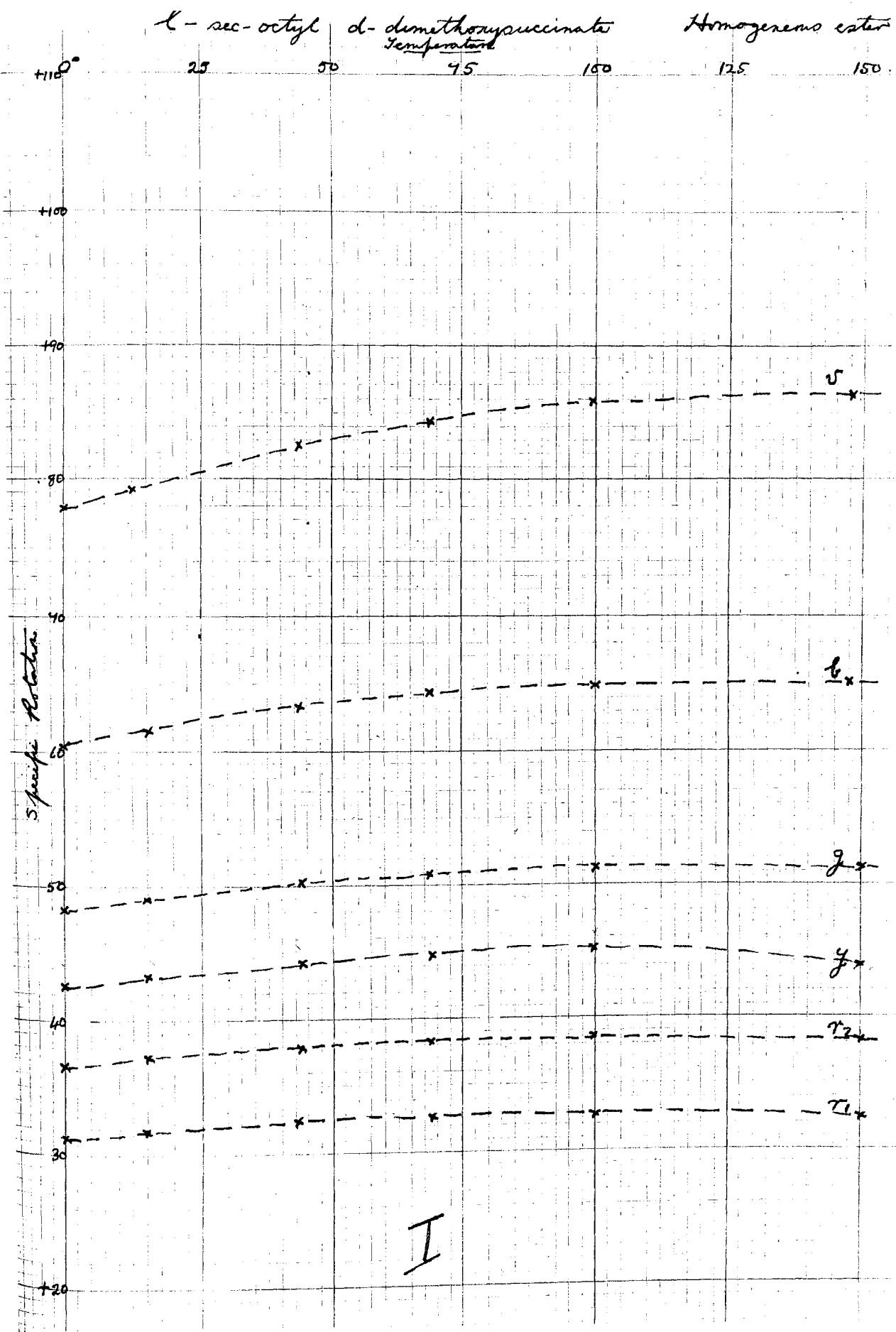
The rotation of this ester decreases (i.e., the negative value decreases) almost linearly with increase of temperature. Solution in o-nitrotoluene increases the magnitude of the rotation at low temperatures, but the rotation decreases much more rapidly with rise of temperature. s-Tetrachloroethane decreases the rotation and also decreases the slope of the T-R curves. These solvents have therefore a similar effect as on the ester above. The curves for this ester are shown in graphs V-VIII.

l-sec-octyl i-dimethoxysuccinate.

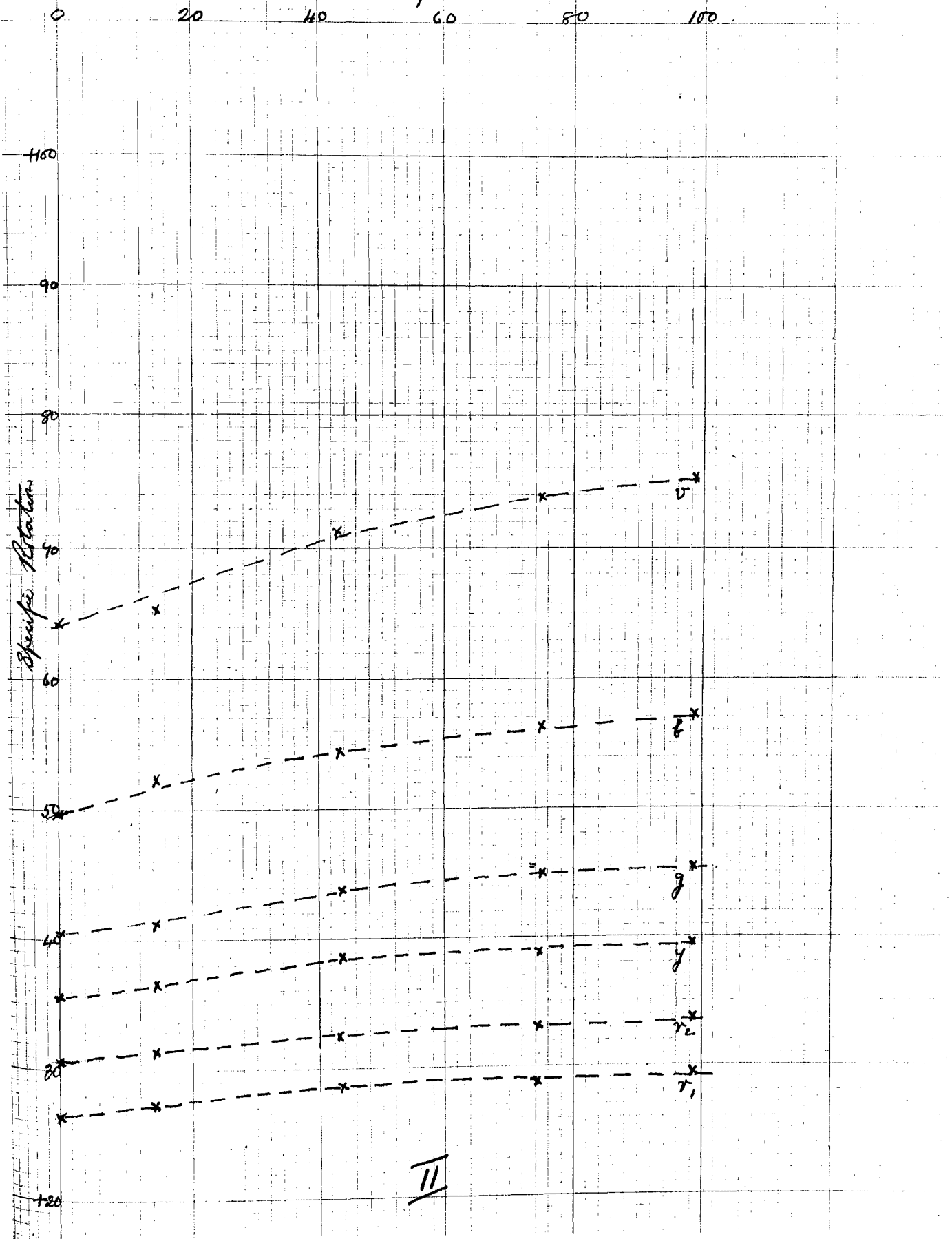
The rotation of the homogeneous ester decreases with rise of temperature, and appears to tend towards a maximum at temperatures above 150°. Solution in o-nitrotoluene in this case decreases the rotation, which now increases with increase of temperature, and would show a maximum above 100° (the maximum appears in the observed rotations). The T.R. curves, for the five different colours of light used, run very closely together towards 0°, and would probably indicate a region of anomalous rotation dispersion below that temperature. S-Tetrachloroethane again decreases the rotation. The curves for this ester are shown in Graphs IX-XI.


l- sec- octyl i. dimethoxysuccinate
Temp:
0
20
40
60
80
100
2
4
6
8
10
12
14
Specific Rotation
Gms. tetrachloroethane
Homogeneous

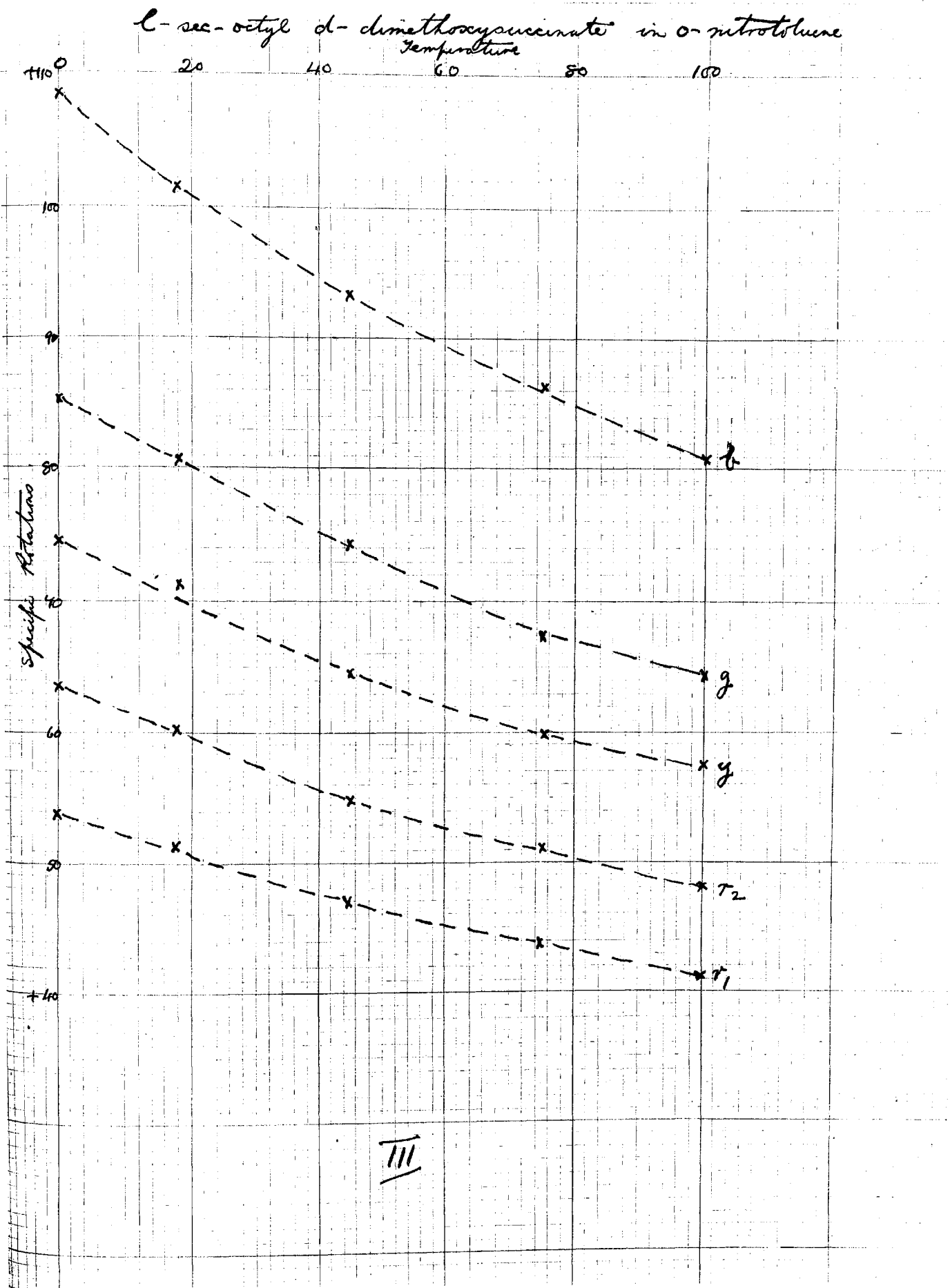
XI


l - sec - octyl d - dimethoxysuccinate
Homogeneous ester
Temperature
+110°
25
50
75
100
125
150
+100
+90
+80
+70
+60
+50
+40
+30
+20
Specific Rotation
v
b
g
y
r2
r1
I

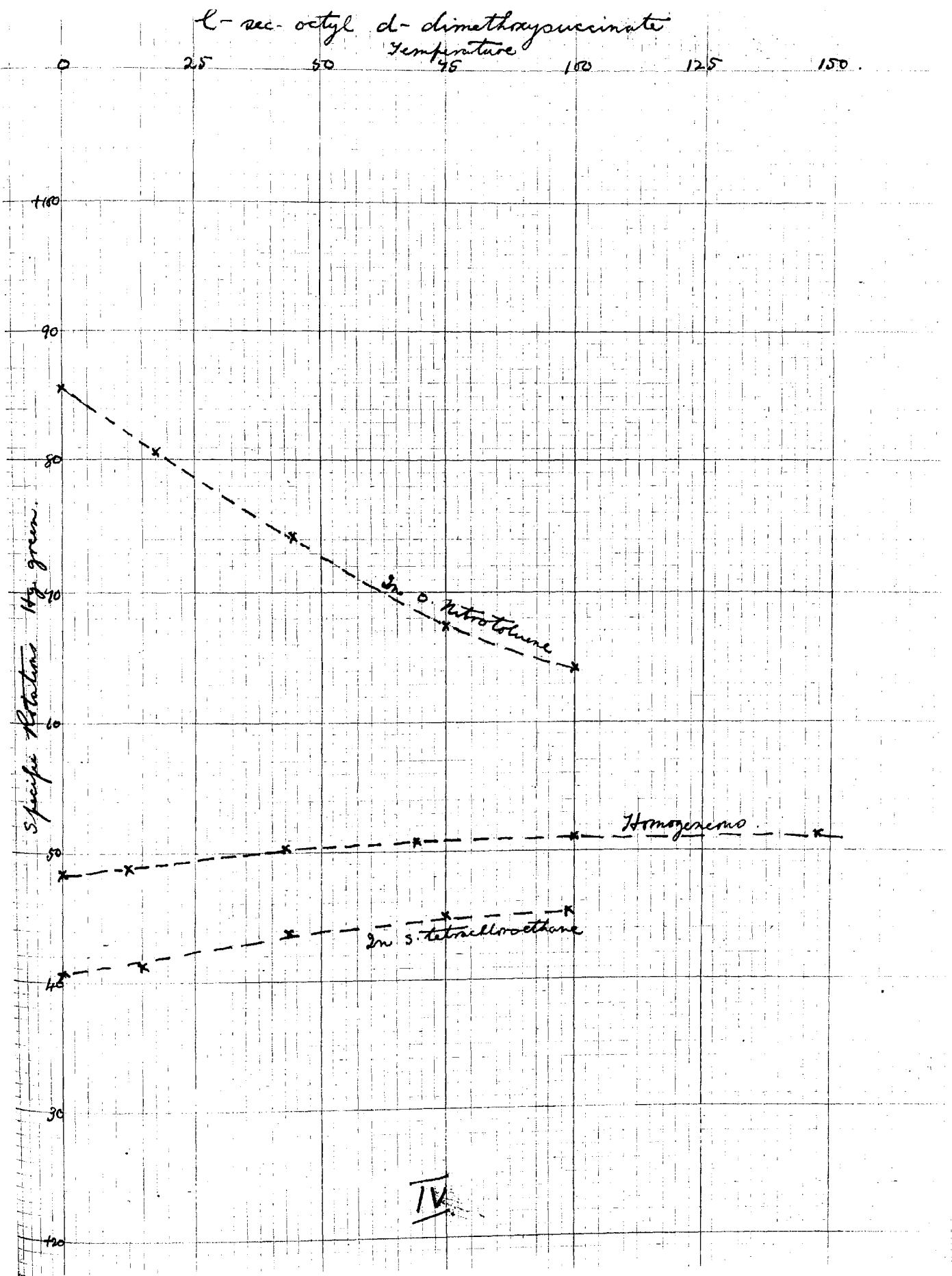
l- sec- octyl d- dimethoxysuccinate in s- tetrachloroethane



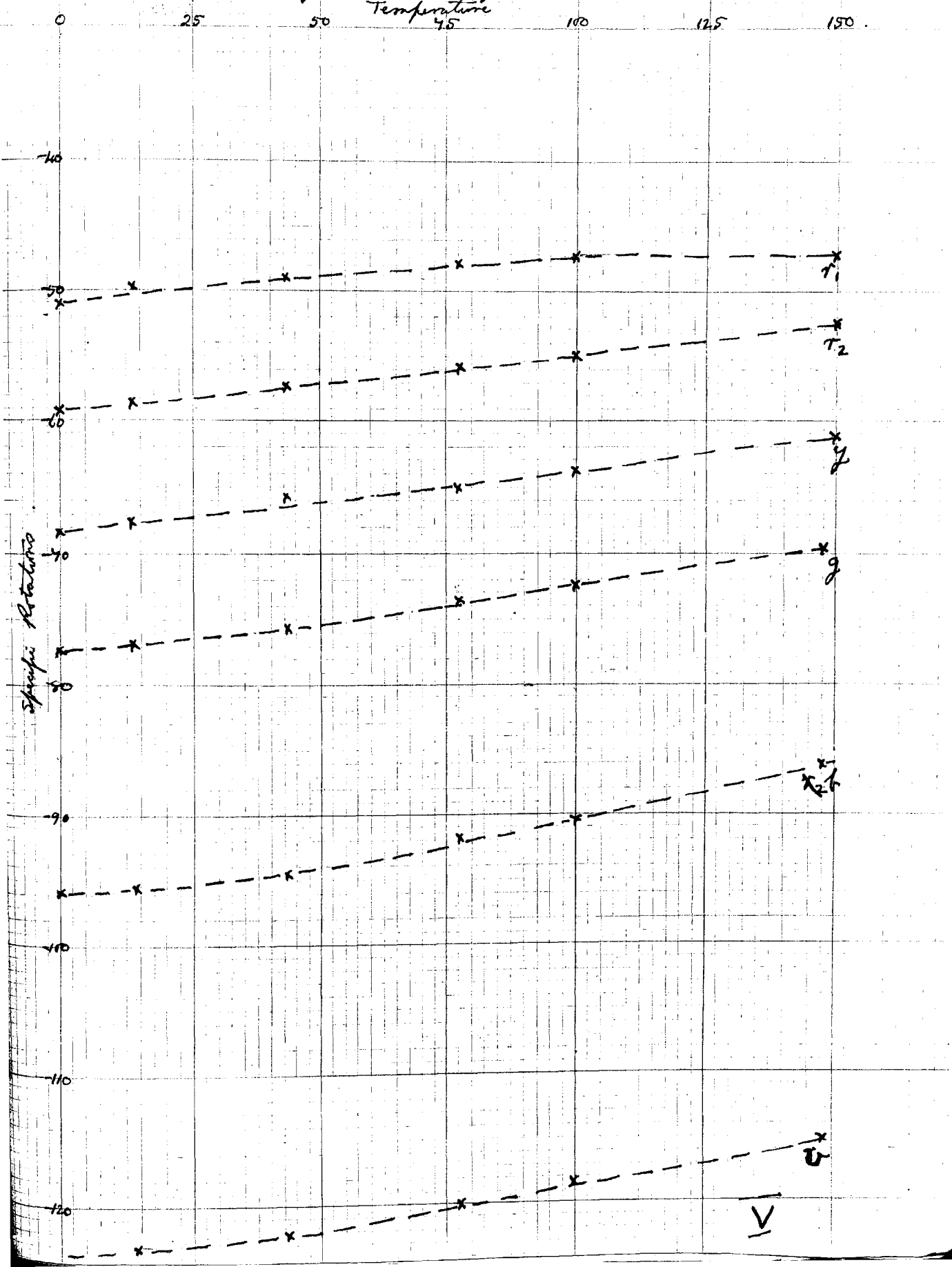
II


l-sec-octyl d-dimethoxysuccinate in o-nitrotoluene
Temperature
+110
0
20
40
60
80
100
100
90
80
70
60
50
+40
Specific Rotation
h
g
y
r2
r1

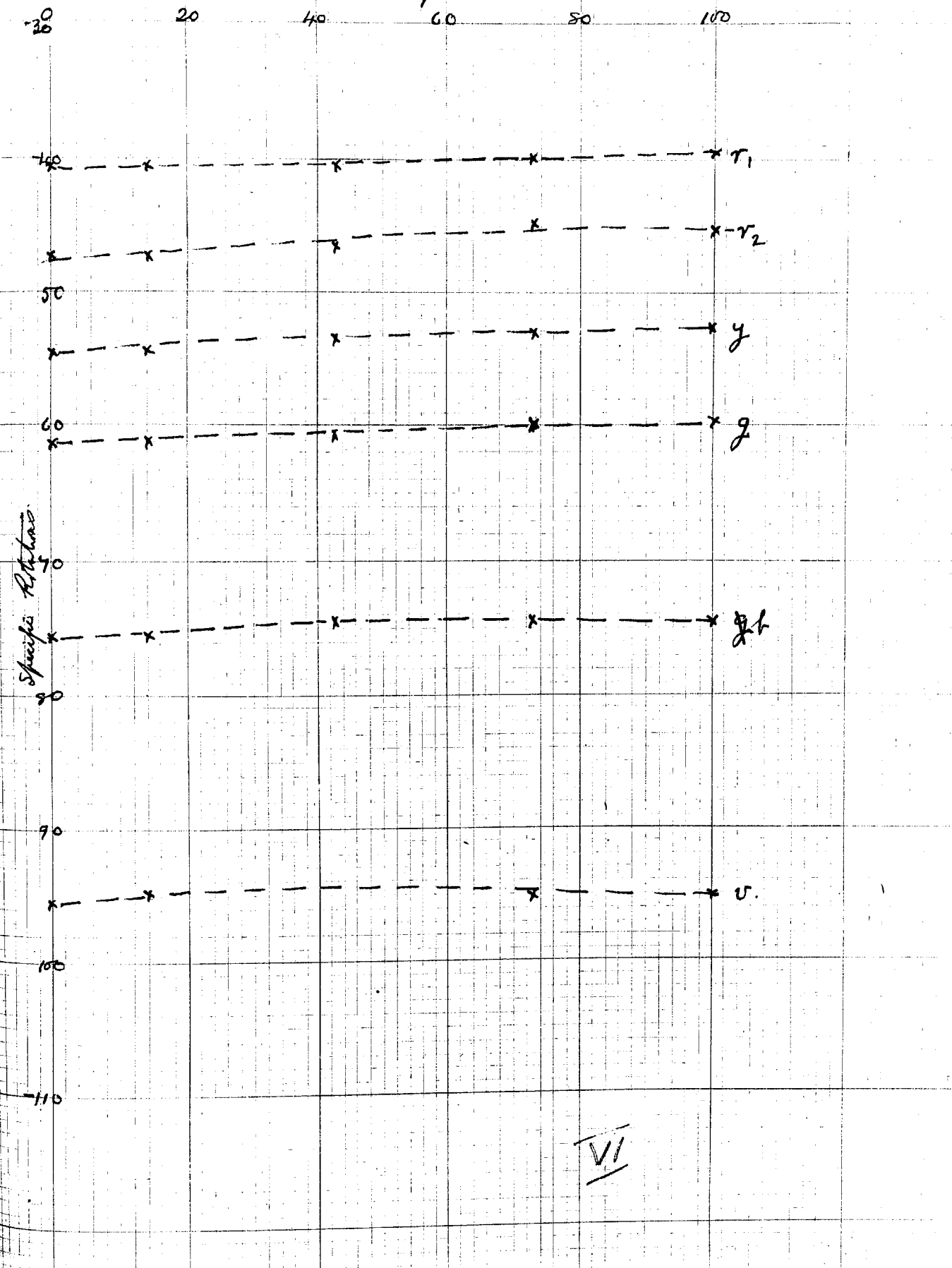
III


l- sec- octyl d- dimethoxysuccinate
Temperature
0
25
50
75
100
125
150
+100
90
80
70
60
50
40
30
20
Specific Rotation Hg green.
In o. Nitrotoluene
Homogeneous
In s. tetrachloroethane
IV.

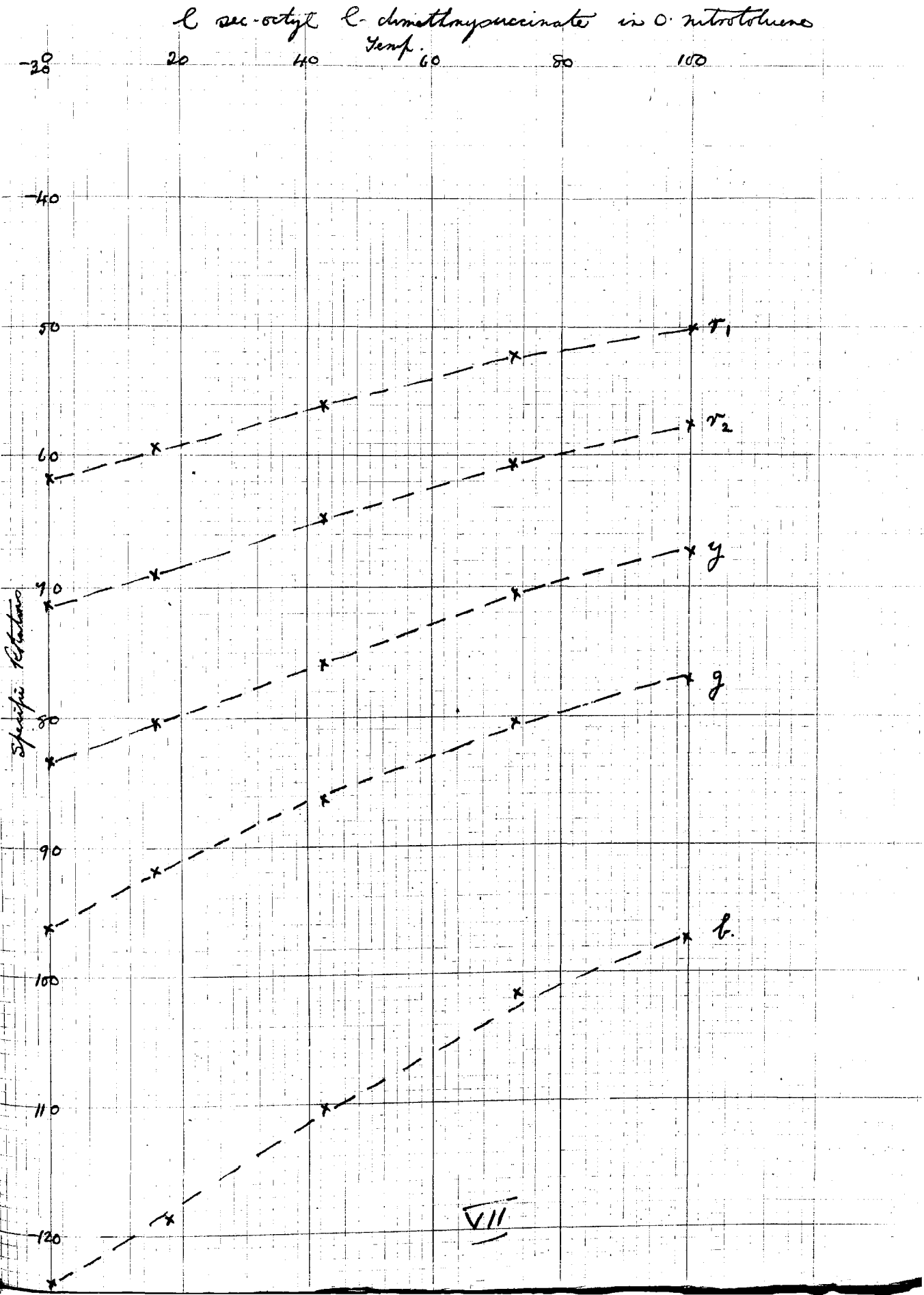
l-sec-octyl l dimethoxysuccinate Homogeneous.



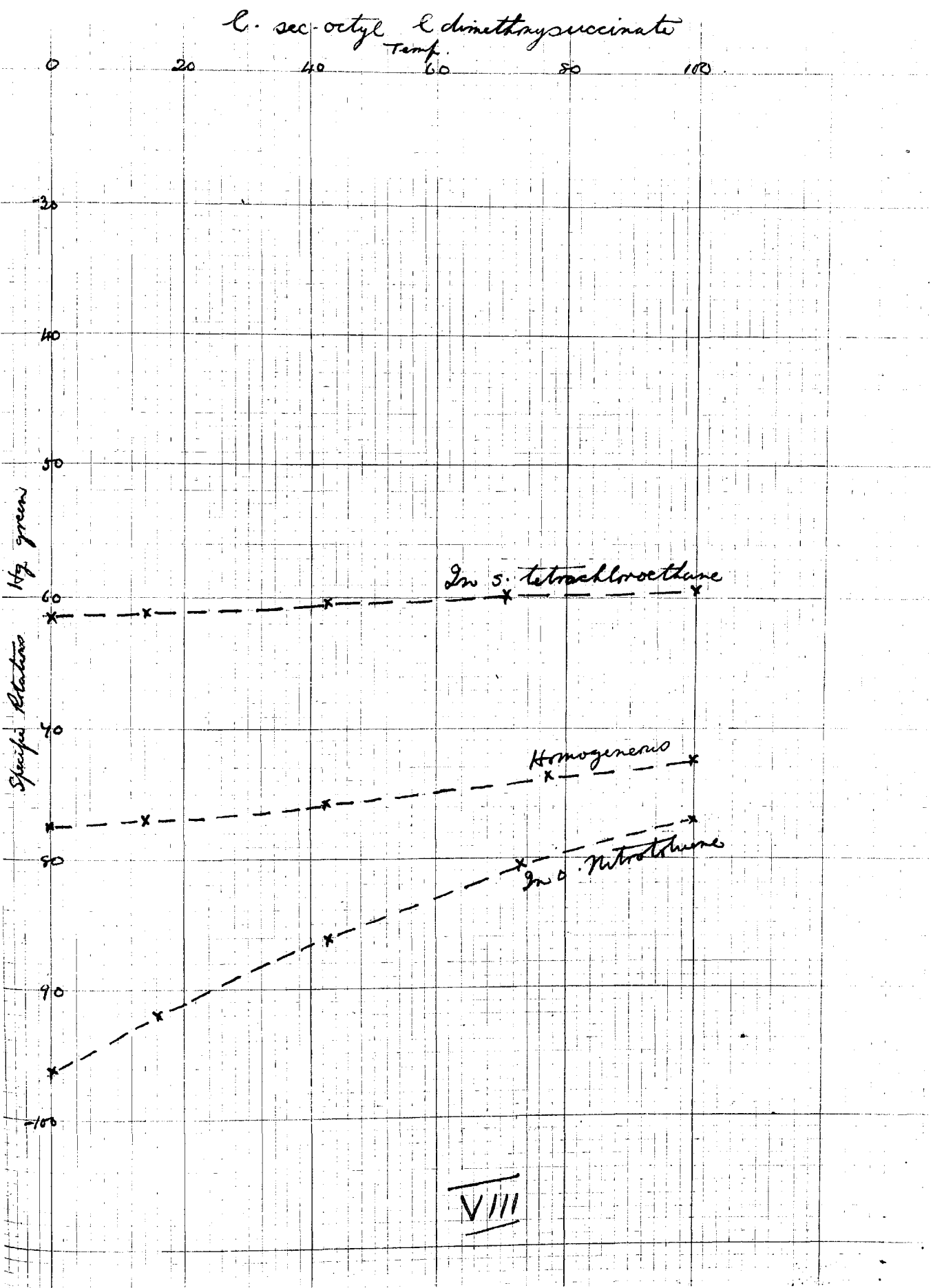
5- Tetrachlorethane Solution of l sec-octyl l-dimethoxysuccinate

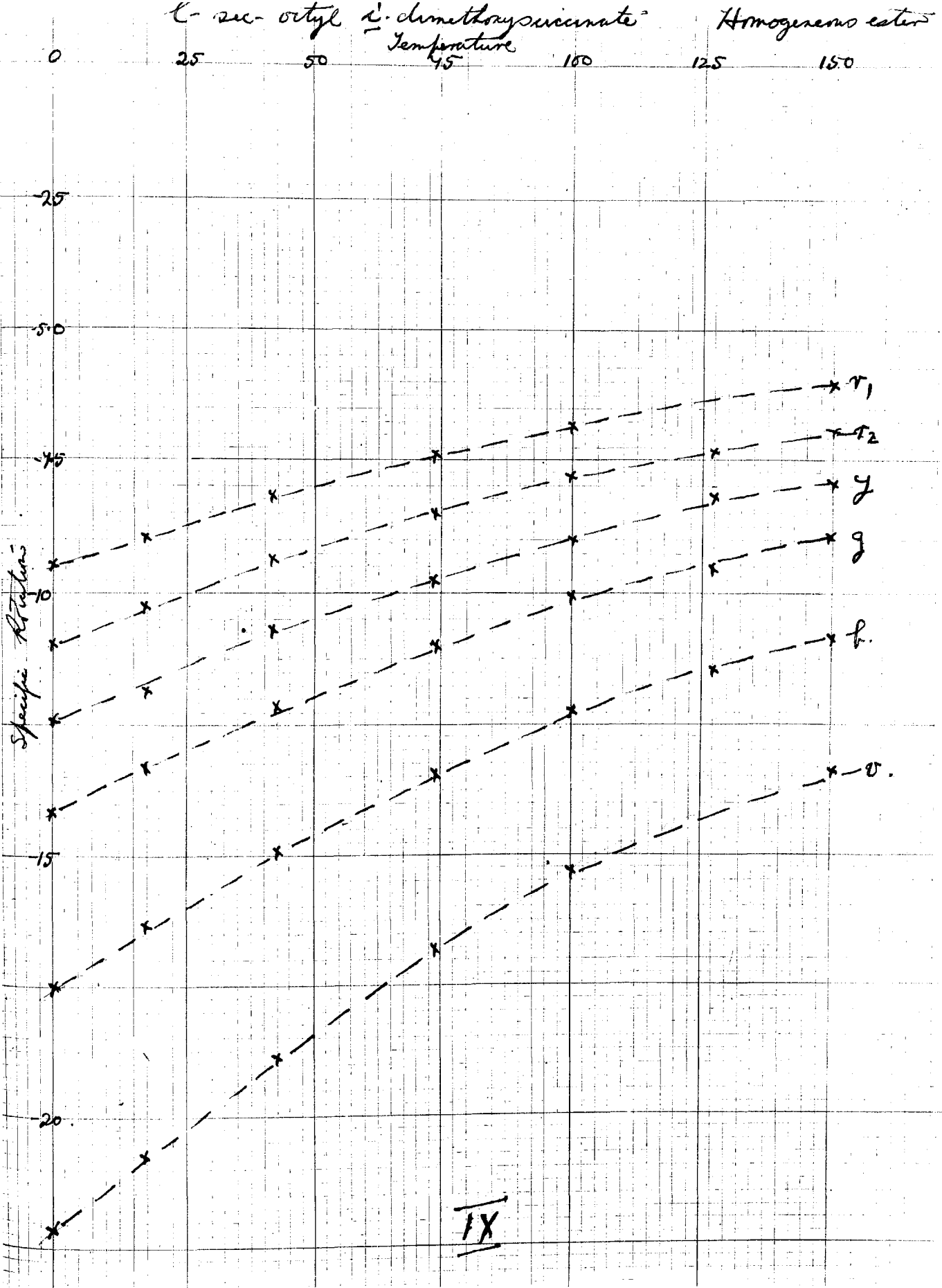


VI

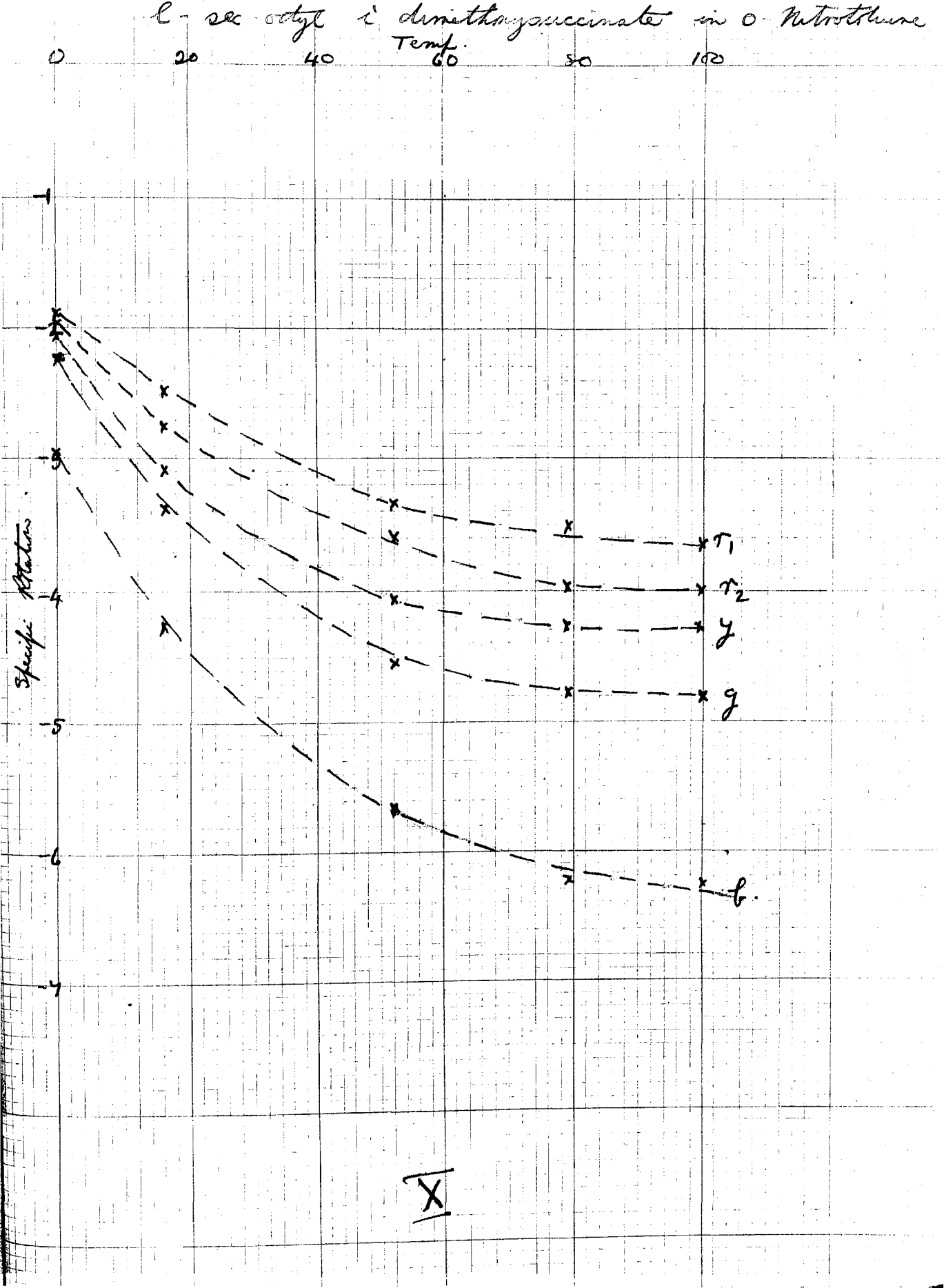

l sec-octyl l-dimethylsuccinate in o-nitrotoluene
Temp.
-20°
20
40
60
80
100
-40
50
60
70
80
90
100
110
120
Specific Rotation
r_1
r_2
y
g
b.

VII


l. sec-octyl l dimethoxysuccinate
Temp.
0
20
40
60
80
100
-30
40
50
60
70
80
90
-100
Mg green
Specific Rotation
In s. tetrachloroethane
Homogeneous
In o. Nitrotoluene
VIII


l-sec-octyl d-dimethoxysuccinate
Homogeneous ester
Temperature
0
25
50
75
100
125
150
-25
-5.0
-7.5
-10
-15
-20
Specific Rotation
r_1
r_2
y
g
b.
v.
IX

l-sec-octyl i dimethoxysuccinate in o-Nitrotoluene



X

NOTES ON THE SEPARATION OF THE AMYL ALCOHOLS FROM FUSEL-OIL

Fermentation amyl alcohol consists of a mixture of iso-amyl alcohol, (2 methyl butan-4-ol $(CH_3)_2CH\text{-}CH_2CH_2OH$) and of the laevo modification of sec-butyl carbinol (2 methyl butan 1.ol $CH_3CH_2CH(CH_3)CH_2OH$); the proportion of the active alcohol varies, being generally from 20-30 per cent. of the total. The separation of these two alcohols, which boil at 131° and 128° respectively, is effected only with considerable difficulty, but has been carried out in several ways.

The first separation (Pasteur, Compt. Rend. 1885, 41, 296) was by recrystallisation of the Barium salts of the amyl hydrogen sulphates. The salt of the l-amyl alcohol is the more soluble, so that recrystallisation gives the salt containing the inactive alcohol, and in order to obtain that in a pure state some 15 to 20 recrystallisations are necessary. The salt containing the active alcohol is obtained from the mother liquors, and it is therefore an extremely difficult operation to obtain the optically pure compound; the evaporation of the mother-liquors must also be carried out at a comparatively low temperature as the barium amyl sulphate is fairly easily hydrolysed, giving barium sulphate with loss of alcohol. By this method Pasteur obtained an alcohol having the rotation αj (500 mms) = -20° (corresponding to

α_D (100 mms) = -3.55°). Other authors repeated Pasteur's method of separation but Marckwald (Ber. 1901, 34, 480) points out that in no case was the rotation of the active alcohol obtained so high as was that obtained by Pasteur himself. [Bakhoven (Pogg. Ann. VI, 325) claims to have obtained a dextro alcohol, using a modification of this method, but his work was repeated by Le Bel (Bul. Soc. Ch. (2), 25, 199) without success].

Another method of separation is described by Le Bel (Compt. Rend. 77, 1021; Bul. Soc. Chem. 1874 (2) 21, 542 and 1876, 25, 545), and consists in acting on the hot mixed alcohols with hydrogen chloride. The iso-amyl alcohol is converted into the chloride more readily than is the active amyl alcohol, and therefore the unchanged alcohol has a higher rotation than the starting product. In this way Le Bel obtained an amyl alcohol - one tenth of original amount - having the rotation α_D(500 mms) = -23.28° (Bl, 25, 545). Rogers (J.C.S., 1893, 63, 1130) by a modification of this method, consisting of heating the alcohols with concentrated aqueous hydrochloric acid in sealed tubes at 100° for some time, recovering the alcohol, and repeating the process, obtained finally an alcohol having the rotation α_D(200 mm) = -8.5°. This method does not appear to be any improvement on that of Le Bel.

Marckwald (loc. cit) shows that even if by Le Bel's method

one could obtain pure l-amyl alcohol only a very small yield could be expected (e.g., the yield of 96% pure alcohol was only one tenth of original amount taken), but that this method might be used to obtain from a weakly-rotating alcohol a product containing from 60-80 per cent. of the active alcohol. Marckwald also points out that the difficulty of separation by Pasteur's method is due to the formation of mixed crystals, and Marckwald and McKenzie (Ber., 1901, 34, 485) describe a method of separation by converting the alcohols into the acid esters of 3-nitrophthalic acid and recrystallising these compounds. Here again the separation is difficult as mixed crystals are formed. To obtain the active alcohol the commercial product is first of all treated, by Le Bel's method, with hydrogen chloride until a more strongly rotating alcohol is obtained. The acid ester of 3-nitrophthalic acid from this is mixed with its own volume of carbon disulphide and the residue recrystallised from benzene until the melting point is 113.5-114.5°. In this way Marckwald and McKenzie obtained l-amyl alcohol having the rotation $[\alpha]_D^{20}$ = -5.90°, which corresponds to an observed rotation of α (200 mms) = -9.62°.

It will be seen from the above that the separation of these two alcohols is extremely difficult. When it is considered that we are here concerned with the separation of structural isomers, and that the stereoisomeric forms of some of the optically active

alcohols can be separated with comparative ease from the inactive mixture (e.g., the resolution of the sec-octyl alcohol required for the experiments described in the first part of the paper is fairly easy), it would appear probable that some method might be found which would give a much more satisfactory separation. Several attempts have therefore been made to separate the alcohols by crystallisation of alkaloid salts of the amyl hydrogen sulphates and of the amyl hydrogen phthalates; but so far without success.

To obtain for a starting product an amyl alcohol richer in the active alcohol than that obtained from fusel-oil the method of Chapman & Smith was tried. (Proc. Roy. Soc. Lond. 1869, 17, 308, also Chapman J.C.S. 1870, 23, 96). These authors state that a separation may be effected to a certain extent by boiling the mixture of alcohols with caustic soda (or calcium chloride, potassium acetate etc.), and distilling the product; the rotation of the first distillate is increased while pure non-rotating alcohol is retained by the caustic soda. Popoff (Ber., 1873, 6, 560) states that treatment with caustic soda causes no increase in rotation, and also Balbiano (Gazetta Chem. Ital. VI, 402) found that this treatment rendered the active alcohol inactive. Moreover, Popoff (loc. cit.) states that by direct fractionating of commercial amyl alcohol a more strongly rotating alcohol may be obtained, and Lachowiecz (Ann. 1883, 220, 171)

confirms this, and claims to have obtained the pure inactive alcohol by simple fractional distillation. Neither of these authors, however, give the increase in rotation obtained. In order to find if the method of Chapman and Smith gave any separation of the alcohols, the increase in rotation on simple fractional distillation with a rod and disc column was compared with the increase in rotation on fractionating with the same column, after boiling under reflux with caustic soda (excess caustic soda over the amount required to give a saturated solution was used). It was found that practically the same increase in rotation was obtained in each case.

The following results are typical:-

250 grams fermentation amyl alcohol were distilled, using a rod and disc column; one third was distilled over and its rotation observed (B. Pt. 128-131°). This was poured back, and again distilled after boiling with 40 grams of caustic soda. About one third of the alcohol was again collected (B. Pt. 100-131°), dried with K_2CO_3*, redistilled, and its rotation observed.

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*On distillation after boiling with caustic soda (or potash) the first distillate always contains water, the first 10 ccs. or so separating into two layers. The sodium replaces the hydrogen of the alcohol. If as much of the alcohol as possible is distilled off the residue solidifies, and when this is diluted with water, and distilled, a mixture of alcohol and water is obtained. This alcohol is almost inactive, due to the racemisation of the active alcohol which it contains, as is proved by mixing all the fractions, from a distillation with NaOH, when it is found that the rotation has been diminished. Le Bel (Bul. Soc. Chem. (2) 31, 104) found that l-amyl alcohol is made inactive by converting (Contd.)

In each case the rate of distillation was approximately the same.

Length of tube = 400 mms.

For these, and for the other rotation values given in this part of the paper, yellow light was used (λ = 5790). This was obtained from a Nernst lamp, and was made to correspond with one of the yellow lines of the mercury spectrum (for method see Patterson J.C.S. 1916, 109, 1143).

Simple Fractional Distillation:

250 grams having rotation -5.535° gave 90 grams with rotation -5.755°.

Distillation with caustic soda:

The same 250 grams after boiling with 40 grams NaOH gave 93 grams having the rotation -5.77°.

The same experiment was tried, using caustic potash in place of caustic soda.

350 grams alcohol with rotation -3.72° gave 70 grams with rotation -4.54°.

The same 350 grams, after boiling with 92 grams KOH gave 76 grams with rotation -4.035°.

(Contd.)
it into sodium amylate and heating for some time to a high temperature. From this racemic mixture he obtained the dextro alcohol by allowing certain fungoid growths to propagate in it for a time.

These results show that the use of caustic soda or caustic potash does not cause any greater increase in rotation than can be obtained by simple fractional distillation. Practically non-rotating alcohol is indeed retained by the caustic soda, but this is due to the racemisation of the active alcohol. The following distillation, using a longer column with air-jacket, shows that a considerable increase in rotation may be obtained by very careful fractionation without the use of caustic soda.

About 600 grams were used. Original Rotation -4.635°.

		B. Pt.	Rotation (400 mms).
1st fraction	87 grams	128-130°	-5.58°
2nd "	134 "	130-131°	-5.40°
3rd "	153 "	131°	-4.87°
4th "	224 "	131°	-3.70°

To attempt to find a more suitable method for the separation of these alcohols, the following salts were prepared.

QUININE SALT OF AMYL HYDROGEN SULPHATE

Barium amyl sulphate was first prepared, according to the method of Pasteur (C.R. 41, 296) from amyl alcohol having the observed rotation α_{5790}(400 mms) = -5.8°. The alcohol was recovered from a sample of the well-mixed crystals, and was found to have the rotation α_{5790}(400 mms) = 4.62°; some of the active alcohol was probably lost owing to the decomposition of the barium salt on evaporating the mother liquors.

The quinine salt was prepared by adding a solution of barium amyl sulphate to quinine sulphate (equal mols) suspended in a large volume of hot water. The quinine gradually dissolved and a heavy precipitate of barium sulphate separated to the bottom of the flask. This solution was filtered hot, and, on standing, deposited crystals of quinine amyl sulphate in feathery tufts; various solvents were tried for the recrystallisation, but water was found to be the most suitable. After three recrystallisations the melting-point had risen from 84° to 90°, and the rotation (of a one per cent. solution in a 2 dm. tube) from -2.87° to -3.31° and these remained unaltered on further crystallisation. The amyl alcohol recovered from the recrystallised quinine salt, by steam-distillation with dilute sulphuric acid, after drying with potassium carbonate, distilled at 130°, and gave a rotation of -2.2° in a 4 dm. tube.

On evaporating the mother liquors it was found that the salt decomposed - even on evaporation at the ordinary temperature - and only quinine sulphate was obtained.

The quinine salt has probably the formula

$$\mathrm{Q.}\ \begin{matrix} C_5H_{11} \\ H \end{matrix}\!\!\diagdown\!\!\diagup SO_4 \quad \tfrac{1}{2}\,H_2O.$$

The amount of water of crystallisation was estimated by weighing about 1 gram of the substance on a watch-glass, and drying in a vacuum dessicator over sulphuric acid until the weight

was constant. The percentage of SO_4 was estimated by precipitating as barium sulphate, by boiling the substance for some time with dilute hydrochloric acid and barium chloride under a reflux condenser.

Results:-	Percentage of water	Found	1.73
		Calculated	1.79
	Percentage of SO_4	Found	19.04
		Calculated	19.19

BRUCINE SALT OF AMYL HYDROGEN SULPHATE

This salt was prepared by dissolving barium amyl sulphate in as little hot water as possible, and adding just sufficient sulphuric acid to precipitate the barium as sulphate; this solution was filtered and tested to ensure that there was no excess barium amyl sulphate or sulphuric acid. The calculated amount (equal molecules) of brucine was added, and immediately dissolved, when the solution was again filtered and set aside to crystallise. After a considerable time a mass of hard crystals formed on the bottom of the vessel. The melting point was indefinite, about 86°, and on recrystallisation became 91°, but did not rise on further recrystallisation. The rotation of a one per cent. solution in alcohol in a 200 mm. tube was -0.29°, and remained unchanged on recrystallisation. Water was again found to be the most suitable solvent, the salt being very soluble in most organic

solvents, even in the cold. The alcohol obtained from the recrystallised brucine salt gave a rotation of -5.4° in a 400 mm. tube.

On evaporating the mother liquors the salt decomposed and only brucine sulphate was obtained. The amount of water of crystallisation and of SO_4 was estimated in the same manner as for the quinine salt, and corresponded to the formula B. $C_5H_{11}.HSO_4.2H_2O$.

Percentage of Water		Percentage of SO_4	
Found	6.10	Found	15.80
Calculated from formula	6.02	Calculated	16.06

An attempt was made to prepare cinchomine amyl sulphate in the same manner, but the salt could not be made to crystallise.

The cinchonidine salt of amyl hydrogen sulphate was prepared in the same way as the brucine salt. It gave white crystals from water, melting at 104°. The rotation of a five per cent solution in water in a 200 mm. tube had risen from $\alpha^{18^{\circ}}_{5461} = -11.91^{\circ}$ to $\alpha^{18^{\circ}}_{5461} = -12.27^{\circ}$ after four recrystallisations from water. Sufficient of the salt, which is now being further examined, has not yet been prepared to allow of the recovery of the alcohol.

The separation of the alcohols by means of alkaloid salts of the acid phthalates was also tried. Amyl hydrogen phthalate

was prepared by heating to 120° for 24 hours a mixture of equal molecules of commercial amyl alcohol and phthalic anhydride. The resulting mixture was dissolved in excess sodium carbonate solution, and, after extracting with ether any unchanged alcohol or neutral esters, the acid phthalate was precipitated with dilute hydrochloric acid, and extracted with chloroform. On removing the solvent, the acid phthalate was left as a thick oil, which would not solidify.

The Brucine salt was prepared by dissolving amyl hydrogen phthalate in acetone, and adding an equal molecular proportion of anhydrous brucine; on heating, the brucine dissolved and the solution was filtered. After concentrating the solution to small bulk and cooling, practically the whole mass went solid so that the crystals were with difficulty separated from the mother liquor. Recrystallisation was attempted from various solvents, the salt was extremely soluble in most, but it could be recrystallised by dissolving in as little hot acetone as possible and adding an equal bulk of hot chlorobenzene. After recrystallising four times from this mixture the melting-point was still very indefinite (about 85-90°). The salt was then poured into dilute hydrochloric acid, and the amyl hydrogen phthalate extracted with ether. After removing the ether the acid phthalate was hydrolysed to obtain the alcohol, which had now the rotation $\alpha^{17°}_{\text{Hg green}}$ (100 mm) = -0.42°, the original rotation being about 2°.

It is therefore evident that the brucine salt of the acid phthalate of the iso-amyl alcohol is the least soluble and that this method would not readily give pure l-amyl alcohol.

Attempts to prepare quinine amyl phthalate and cinchonidine amyl phthalate were unsuccessful.
